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Collodial Behavior of "Ludox" Silica Sol

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COLLOIDAL BEHAVIOR OF "LUDOX" SILICA SOL

by

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Approved by J D Porter

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I. General Introduction

"Ludox" silica sol consists of extremely tiny particles of silica dispersed in water and stabilized by a small amount of alkali. The sol is produced by a very interesting ion exchange process; and although the actual process for the production of "Ludox" remains a commercial secret of the E.I. Du Pont Company, the general method of preparation of hydrous oxide sols by exchange methods was described as early as 1944. Ryznar (1) gives the following general method for the preparation of a silica sol by the use of cation exchangers:

Sodium silicate is passed through a cation exchanger and the sodium ion is replaced by hydrogen ion to give:

$$ExH_2 + Na_2SiO_3 = ExNa_2 + H_2SiO_3$$

The effluent has a low concentration of silica (about 2.7% SiO_2) and small amounts of sodium oxide and sodium sulfate. The sol thus formed is not too stable but the stability of the product is greatly increased by the addition of sodium silicate, which increases both the alkalinity and the silica concentration. The original sol, which consists of small condensed units of silicic acid, is clear and colorless but upon standing these particles condense further to give larger ones and the originally clear solution becomes opalescent.

The mechanism of the condensation process involves essentially the splitting out of water between units of silicic acid. In the formation of the final "Ludox" several thousand

of these silicic acid units unite to form a silica micelle of spherical shape. The presence of free surface hydroxyl ions leads to a negative sol and to the proposed structure of the silica micelle shown in Figure 1a.

In Table 1 are listed some physical properties and the approximate chemical composition of "Ludox" silica sol as given by the Du Pont Company (2). These general properties are augmented by further data on the chemical factors affecting "Ludox" in following sections.

Table 1:

Physical Properties and Approximate Chemical Composition of "Ludox"

SiO_2	29 - 31%
Na_2O	.31 - .41%
Sulfates as Na_2SO_4	0.15% Max.
pH	9.5 - 10.5
Specific Gravity °Be	24.7 - 26.4°
Viscosity at 25°C	2.0 - 3.3 cps.
Freezing Point	32°F (silica irreversibly precipitated)

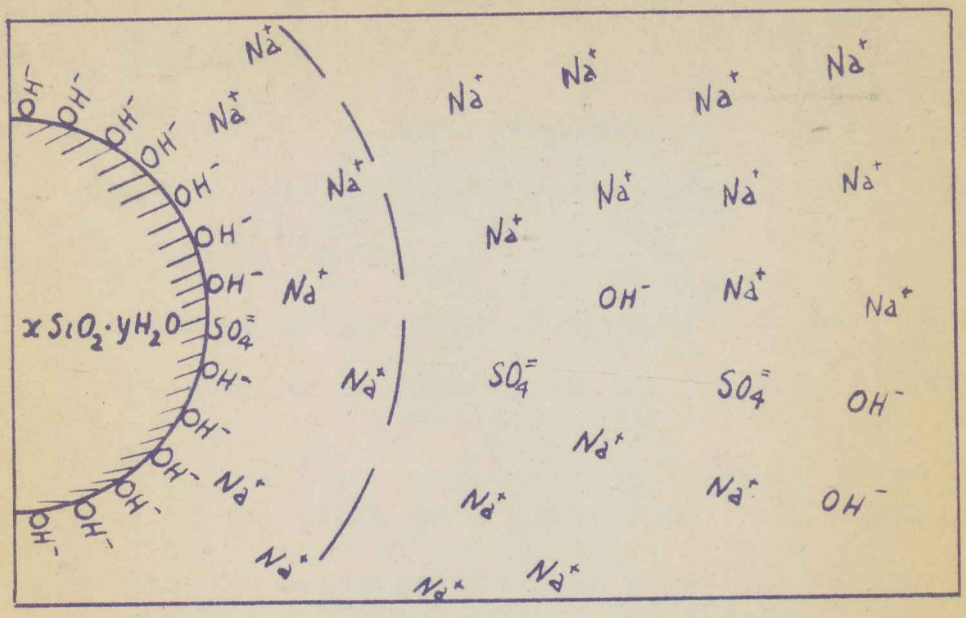
Much of the material of the following sections is presented in terms of the gelation of "Ludox" sol and it might be well to consider at this point a possible mechanism by which gelation occurs. Figure 1a. depicts the probable structure of a silica micelle and shows that the charged particle is definitely negative. This means that positive ions should be effective in gelling the sol and this is brought out in Figure 1b. The latter depicts what happens to a silica micelle when a considerable concentration of potassium chloride is mixed with the sol. Potassium ions enter into the double layer, causing the double layer to contract, and lower the ζ-potential sufficiently to "discharge" the charged particle.

If we think of certain of these charged regions on the silica particles as being particularly activated in some way, then the function of an added electrolyte is to discharge these so-called "active-centers". An extensive network of silica particles linked through their "active-centers" now results which entrains all of the liquid phase and in this way a gel is formed.

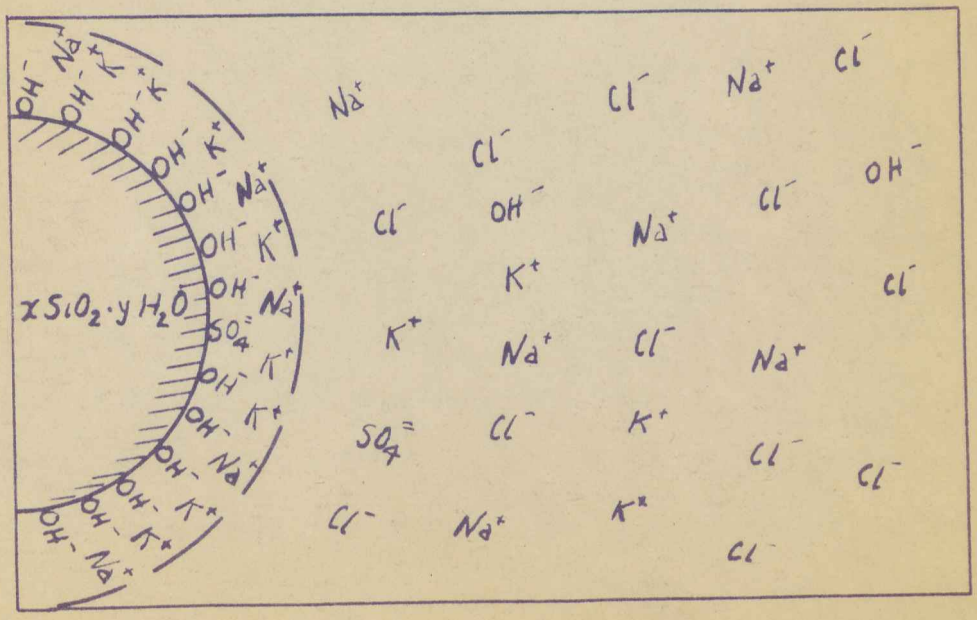
The remaining sections of this study of "Ludox" will be concerned with the description of various aspects of the colloidal behavior of "Ludox" sol. The preliminary nature of this present study of "Ludox" should open up many avenues of approach to future workers in this field and we shall try in some of the following sections to suggest future work.

Figure 1.

a. Silica Micelle



b. Silica Micelle After Addition of KCl



II. Effect of Electrolytes

In studying the effect of electrolytes some of the information sought was:

(1) the concentration of certain electrolytes necessary to cause gelation in a given length of time (1 hour).

(2) the ways in which different electrolytes differ in their effect on "Ludox."

(3) the appearance of the gels after they had been formed.

The first problem is studied in the following manner outlined by Bartell (3):

A series of solutions of a particular electrolyte, differing widely in concentration, is prepared and each of these solutions is mixed with an equal volume of "Ludox." The usual procedure is to pipette 5.00 ml. of a given solution into 5.00 ml. of "Ludox" contained in a test tube and to mix. At the end of one hour the samples are observed to see which ones have gelled and which ones have not. The two adjacent members of this series, one of which causes gelation in less than one hour and the other in more than an hour, are then singled out. A new series of solutions is now prepared all of which have concentrations falling between the two members singled out from the first series. These solutions are now mixed with "Ludox" and observed after one hour. As with the first series, two members are again singled out and a new series of solutions is prepared. And again these solutions are mixed with "Ludox" and observed.

Usually in this third series the concentrations of the various solutions do not differ greatly and one member can be picked out which causes gelation in just one hour. Table 2, which gives data on a complete run for potassium chloride, should serve to clarify the above procedure.

In all cases gelation is taken to be complete when the test tube containing the gel can be inverted and still have the gel adhere to the walls. In the third series of solutions referred to above, that member which causes gelation in just one hour has a concentration which we shall call the "limiting value" for the particular electrolyte. It is important to note here that the concentration designated as the "limiting value" refers to the concentration of the electrolyte <u>after</u> mixing i.e. it is the concentration of the electrolyte in the gelation mixture. In Table 3 are listed the "limiting values" for the various electrolytes that have been studied. "Limiting values" are expressed in millimols per liter.

We might mention that an alternative method for determining these "limiting values" would be to measure the gelation time for a series of solutions and to plot a graph: <u>Gelation Time</u> vs. <u>Concentration of Electrolyte in Gelation Mixture</u>. From this graph the concentration possessing a one hour gelation time could then be determined. This particular method has been used in some of the studies in the following sections.

Table 2:

Limiting Value for KCl

Vol. of 1.00M KCl	Vol. of H_2O	Vol. of Diluted KCl	Vol. of "Ludox"	Conc. of KCl in Mixture (mmols/l.)	Time of Mixing	Results After 1 Hour
First Series						
25.0ml	------	5.00ml	5.00ml	500	3:24	gelation
25.0	25.0ml	"	"	250	3:27	gelation
25.0	50.0	"	"	167	3:28	no gelation
10.0	40.0	"	"	100	3:30	no gelation
Second Series						
10.0ml	10.0ml	5.00ml	5.00ml	250	12:18	gelation
10.0	12.0	"	"	227	12:19	no gelation
10.0	14.0	"	"	208	12:20	no gelation
10.0	16.0	"	"	192	12:21	no gelation
Third Series						
10.0ml	10.2ml	5.00ml	5.00ml	248	11:43	gelation
10,0	10.4	"	"	245	11:44	no gelation
10.0	10.6	"	"	243	11:45	no gelation
10.0	10.8	"	"	240	11:46	no gelation
10.0	11.0	"	"	238	11:47	no gelation

Limiting Value for KCl = 243 millimols/l.

Table 3:

Limiting Values for Various Electrolytes

Electrolyte	Limiting Value in Terms of Conc. of Cation	Electrolyte	Limiting Value in Terms of Conc. of Cation
LiCl	~ 900	$MgCl_2 \cdot 6H_2O$	18.5
NaCl	365	$MgSO_4 \cdot 7H_2O$	18.9
NH_4Cl	240	$BaCl_2 \cdot 2H_2O$	22.7
KCl	243	$CaCl_2$	23.1
K_2SO_4	338	$AlCl_3 \cdot 6H_2O$	17 - 20
$K_4Fe(CN)_6 \cdot 3H_2O$	416	$FeCl_3 \cdot 6H_2O$	25 - 26.4
		$Cr(NO_3)_3 \cdot 9H_2O$	21 - 25
		$CrCl_3 \cdot 6H_2O$	22.5 - 27.5

Conditions under which determinations were made:

Conc. of SiO_2 in the sol $\simeq$ 30%

Conc. of SiO_2 in the gels $\simeq$15%

pH of the sol = 9.8

Temperature = $25 \pm 3^{\circ}C$

Accuracy of results = 1 - 2%

In Table 3 perhaps the most noticeable feature is the difference that exists between electrolytes containing univalent cations and those containing multivalent ones, the multivalent cations being more effective in causing gelation. This is in agreement with the Schulze-Hardy rule (4) which states that the ion opposite in charge to the sol is the effective ion in coagulating the sol and the greater the charge on this ion, the greater will be its precipitating power. For some reason which is not altogether apparent, however, the expected difference in the gelation power between di- and trivalent cations is not to be found in the gelation of "Ludox" although such a difference does exist between uni- and multivalent cations.

Next we can compare the electrolytes of the type MCl where M is Li, Na, K, or NH_4. Upon arranging these electrolytes in the order of their gelling powers (remembering that the lower the "limiting value" for an electrolyte the greater its gelling power) we have: $NH_4 = K > Na > Li$. This is a typical Hofmeister series, which has as its theoretical basis the extent of hydration of ions. In general it is noticed with hydrophobic sols that those ions which are least hydrated tend to have the greatest precipitating power. A general series for the precipitating power of univalent cations for such sols is (5): $Cs > Rb > K > Na > Li$ with the reverse order ($Li > Na > K > Rb > Cs$) for the degree of hydration. Thus our data for the gelling power of electrolytes of the type MCl is explained on the basis of a hydration factor.

A third feature that is apparent from Table 3 is the effect of anions upon the sol. Since "Ludox" is a negative sol, we should expect anions to add to its stability and the greater the charge on the anion the greater should be its stabilizing power. Comparing the electrolytes, potassium chloride, potassium sulfate, and potassium ferrocyanide it is seen that with increasing charge on the anion the "limiting value" also increases (i.e. the gelling power decreases). Since in each case the cation present is the same, the differences must be attributed to the anions and we can arrange the stabilizing power of these anions in the order $Fe(CN)_6^{-4} > SO_4^{=} > Cl^-$.

The "limiting values" for the trivalent cations are recorded in Table 3 as a range of values. With aluminum chloride and ferric chloride gelation occurs very rapidly or not at all. With any concentration of aluminum chloride in the gel of greater than .020M gelation occurs very rapidly and the range indicated as the "limiting value" (17-20) is the range of concentrations of aluminum chloride in which the first gels are formed. Ferric chloride, chromium nitrate and chromium chloride only cause gelation in the narrow ranges indicated as the "limiting value". These electrolytes will be considered in greater detail in Section III. on "irregular series".

The appearance of the gels depends to a large extent upon the type of electrolyte used. The electrolytes containing

a univalent cation produce stiff, soapy-white, opaque gels ($K_4Fe(CN)_6$ gives light-yellow gels). The gels show some syneresis and may be kept for a considerable length of time in a tightly-stoppered tube without cracking. Electrolytes containing divalent cations produce gels which are much less opaque when the concentration of the cation is near the "limiting value." With high concentrations of these electrolytes precipitates and soft white gels are formed. The gels formed under these conditions are more like gelatinous precipitates since a considerable amount of liquid is left uncombined.

Aluminum chloride in high concentrations (.02 to 1.0M) produces precipitates which set to fairly-stiff white gels. In lower concentrations small amounts of silky, white precipitates, but no gels, are formed. Ferric chloride, in the narrow range where gelation occurs, produces soft, orange-colored gels, and at lower concentrations it gives silky precipitates similar to those formed with aluminum chloride. Gels formed by chromium nitrate and chromium chloride are stiff, green ones.

III. "Irregular Series" - Charge Reversal

The cations, Cr^{+++} and Fe^{+++}, illustrate an "irregular series" in their gelation of "Ludox". In general when we speak of an "irregular series" in connection with the coagulation of a sol we mean that in the presence of certain electrolytes there exist successive zones of stability and coagulation for the sol. This phenomenon is usually brought about by multivalent ions and is a result of the reversal of the charge on the sol. (6) The zones of stability and gelation for some trivalent cations on "Ludox" are given in Table 4 and in graphical form in Figure 2.

Taking chromium nitrate as an example and referring to Figure 2 we can trace out an "irregular series" for this electrolyte. In Figure 2 we have plotted inverse gelation time against the concentration of electrolyte in the gelation mixture. The inverse gelation time is obtained by taking the reciprocal of the gelation time in hours in the manner shown in Table 4. Thus a value of zero for the inverse gelation time indicates that the sol is stable indefinitely and the larger the value for this function the more rapidly gelation occurs. In very low concentrations chromium nitrate has no effect upon the sol. In the narrow concentration region where the curve rises to a maximum, chromium nitrate causes "Ludox" to gel and at higher concentrations of chromium nitrate the sol is again stable.

This "irregular series" is explained on the basis of a reversal of charge on the silica micelles. In regions with a low concentration of chromium nitrate there are insufficient chromium ions to discharge the "active-centers" on the silica particles, hence no gelation. In the narrow concentration range enough chromium ions penetrate the double layers of the micelles to neutralize the "active-centers" and gelation occurs. With larger concentrations of chromium nitrate, chromium ions penetrate the double layer to a large extent without discharging the "active-centers". In fact they enter into the double layer to such an extent that they reverse the sign on the charged particle, i.e. in this case there is an excess of positive over negative charges and an individual micelle takes on the appearance depicted in Figure 3a.

Chromium chloride and ferric chloride gives results very similar to chromium nitrate with the exception that ferric chloride causes gelation very rapidly in the range where gelation does occur. Figure 3b is an illustration of a silica micelle reversed in charge by ferric chloride. Data on aluminum chloride have also been included in Table 4 and in Figure 2, and it is interesting to note that no "irregular series" is obtained with this electrolyte. However under the conditions of these experiments we should expect aluminum hydroxide to precipitate out very easily, and the precipitates and gels formed in so many of these cases may consist, at least in part, of aluminum hydroxide. Future analysis of some of these "Ludox-$AlCl_3$" mixtures should prove very enlightening in clearing up some of the effects of the aluminum ion.

Table 4:

Effect of Trivalent Cations

$Cr(NO_3)_3 \cdot 9H_2O$			$CrCl_3 \cdot 6H_2O$		
Concentration of $Cr(NO_3)_3$ in Final Mixture (millimols/l.)	Gelation Time (hrs.)	Inverse Gelation Time ($hrs.^{-1}$)	Concentration of $CrCl_3$ in Final Mixture (millimols/l.)	Gelation Time (hrs.)	Inverse Gelation Time ($hrs.^{-1}$)
1.2	no gelation	0			
17.8	72	.014			
19.2	7-8	.125-.14			
20.0	3	.33	19.2	50	.02
20.8	1.42	.71	20.8	8-10	.10-.125
21.7	1	1	22.7	1.08	.93
22.7	.83	1.20	25.0	.67	1.50
23.8	1	1	27.8	1.17	.86
25.0	1.33	.75			
26.3	22	.046			
27.0	350	.003			
500	no gelation	0			

Concentration of SiO_2 in the final gels $\simeq$ 15%

Temperature = 25±3°C

Table 4:

Effect of Trivalent Cations (Cont'd)

$AlCl_3 \cdot 6H_2O$

Concentration of $AlCl_3$ in Final Mixture (millimols/l)	Gelation Time (hrs.)	Inverse Gelation Time (hrs)
3.2	no gelation	0
16.7	ppt forms instead of gel	0
20.0	rapid gelation	very large
1000	rapid gelation	very large

$FeCl_3 \cdot 6H_2O$

Concentration of $FeCl_3$ in Final Mixture (millimols/l)	Gelation Time (hrs.)	Inverse Gelation Time (hrs)
1.0	no gelation	0
17.8	ppt forms instead of gel	0
19.2	rapid gelation	very large
25.0	rapid gelation	very large
26.3	no gelation	0
500	no gelation	0

Concentration of SiO_2 in the final gels $\simeq$ 15%

Temperature = 25° 30°C

Figure 2.

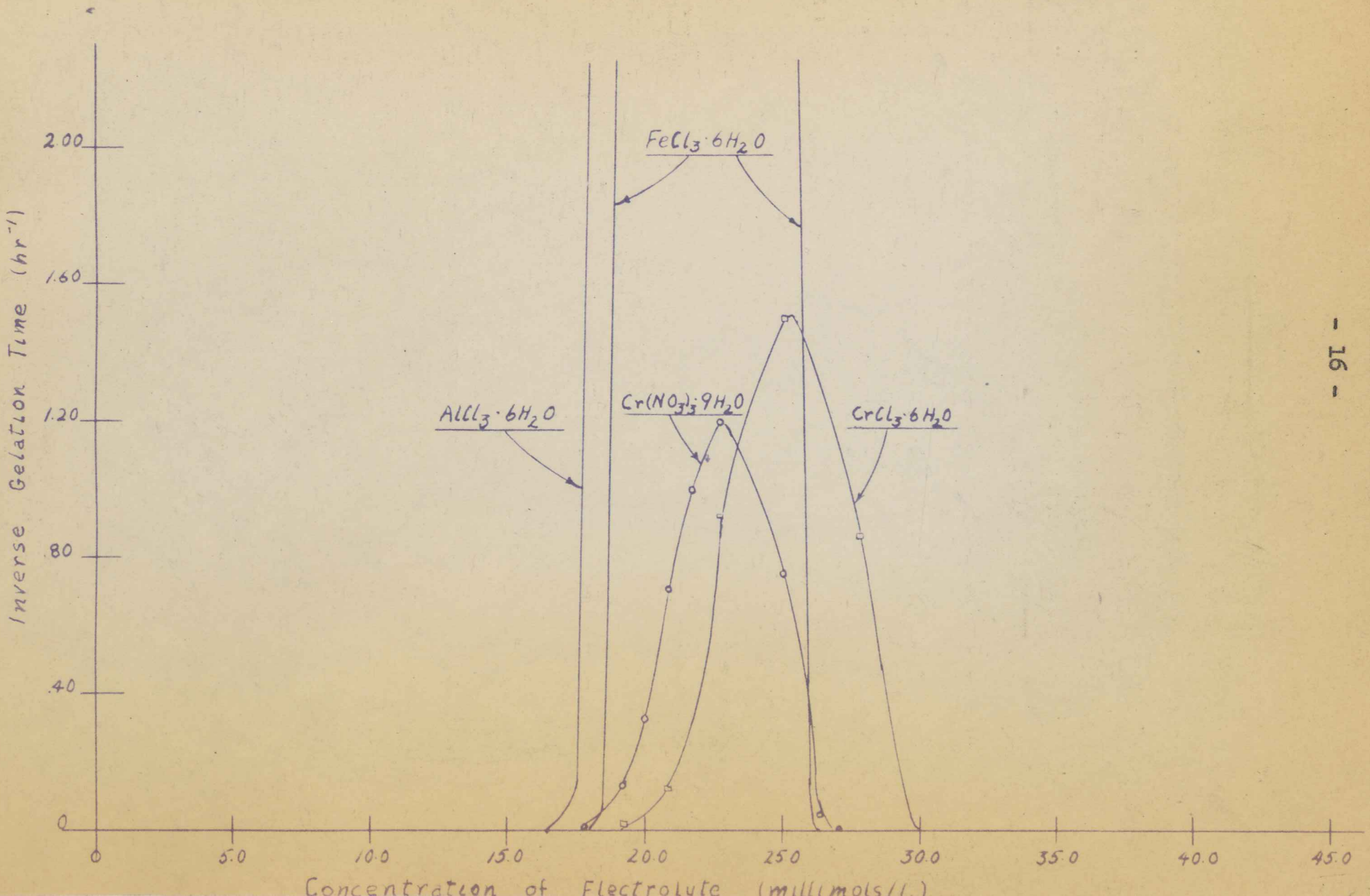
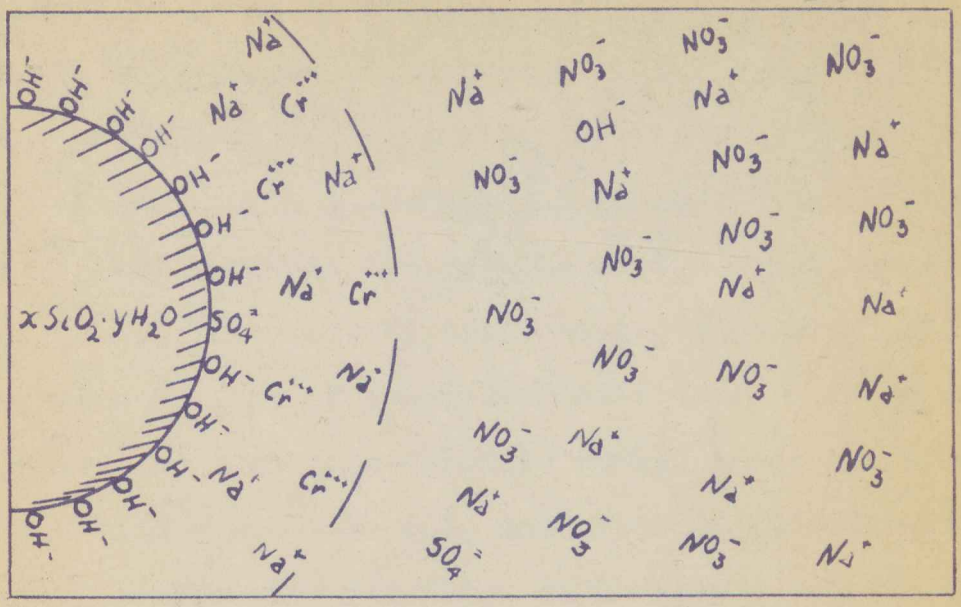
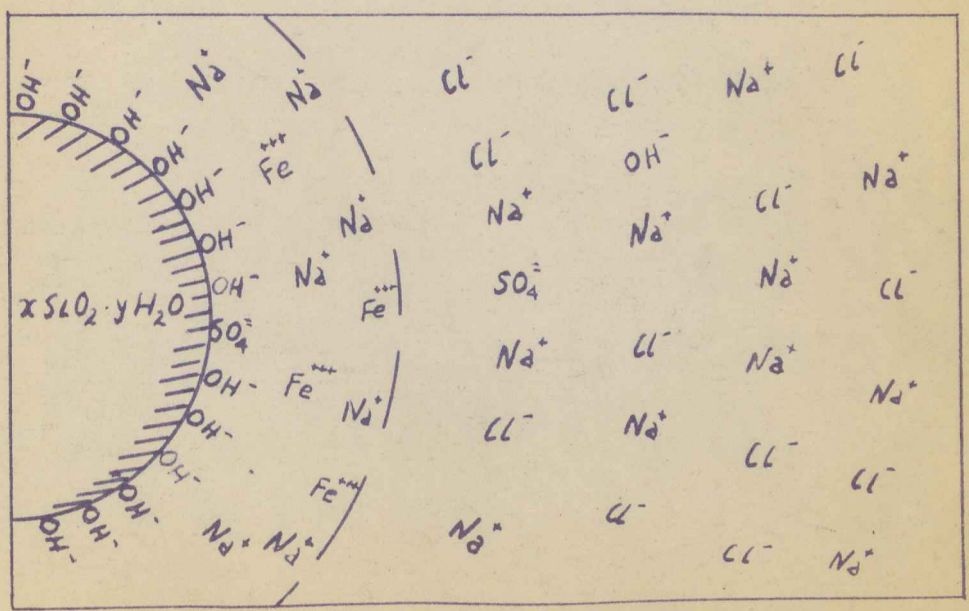

Concentration vs Inverse Gelation Time
Inverse Gelation Time (hr^{-1})
2.00
1.60
1.20
.80
.40
0
$FeCl_3 \cdot 6H_2O$
$AlCl_3 \cdot 6H_2O$
$Cr(NO_3)_3 \cdot 9H_2O$
$CrCl_3 \cdot 6H_2O$
0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
Concentration of Electrolyte (millimols/l.)

Figure 3.

a. Silica Micelle Reversed by $Cr(NO_3)_3 \cdot 9H_2O$



b. Silica Micelle Reversed by $FeCl_3 \cdot 6H_2O$



If charge reversals actually occur in the "irregular series" with trivalent cations then there should be some way in which to verify this experimentally. In the present study two methods have been used to establish this fact. The first method involves gelation studies on the sols which are believed to be reversed. The idea here is to use two electrolytes, one containing a divalent cation and the other a divalent anion, and to see which ion is effective in causing gelation. Table 5 lists the results of two experiments on reversed sols. The electrolytes used are magnesium chloride and potassium sulfate of equal concentrations. If the sols are negative the magnesium chloride should cause the more rapid gelation. With a positive sol, potassium sulfate should bring about gelation the most rapidly. Although the results on the "Ludox-$FeCl_3$" sol are not conclusive, the "Ludox-$Cr(NO_3)_3$" sol is seen to have a positive charge. (Note that the concentrations of the electrolytes, $Cr(NO_3)_3$ and $FeCl_3$, are chosen so as to be on the high side of their respective gelation ranges).

Table 5: Gelation Studies on "Reversed" Sols

"Ludox-.055M $Cr(NO_3)_3 \cdot 9H_2O$"

Concentration in Final Mixture	Results
.250M $MgCl_2$	gelation: 2wks.
.250M K_2SO_4	gelation; 36hr.

"Ludox-.067M $FeCl_3 \cdot 6H_2O$"

Concentration in Final Mixture	Results
.250M $MgCl_2$	no change
.250M K_2SO_4	floc. ppt. after several weeks

NOTE: Concentration of SiO_2 in the final mixtures $\simeq 7.5\%$

The second method for determining a charge reversal with chromium or ferric ion is termed electrophoresis and involves the migration of charged particles in an electric field. Figure 4 gives a diagram of the apparatus required for making electrophoretic measurements. The procedure followed is essentially this:

A small volume of a dilute electrolyte solution (about .005M) is poured into the U-tube. The electrolyte used is sodium hydroxide when studying the original "Ludox" sol, chromium nitrate when studying "Ludox-$Cr(NO_3)_3$" sols and ferric chloride for the "Ludox-$FeCl_3$" sols. Then some of the sol which is being studied is poured into the thistle tube and slowly allowed to enter the U-tube by adjustment of the clamp. The sol forces the electrolyte up the tube and in this way a boundary is formed between the sol and the electrolyte in each arm. The position of each boundary is noted with respect to the attached scale. Now an electric field is applied by means of the electric circuit shown in Figure 4. The charged particles, finding themselves in an electric field, begin to move and hence the boundaries move.

Table 6 gives data on the electrophoretic movement with a "Ludox-$Cr(NO_3)_3$" sol and from these data the charge on the sol is again seen to be positive. By similar electrophoretic measurements the sign on the "Ludox-$FeCl_3$" sols is also shown to be positive. "Ludox" itself turns out to be negative by electrophoresis.

Table 6:

Data on the Electrophoresis of a "Ludox-.033M $Cr(NO_3)_3$" Sol

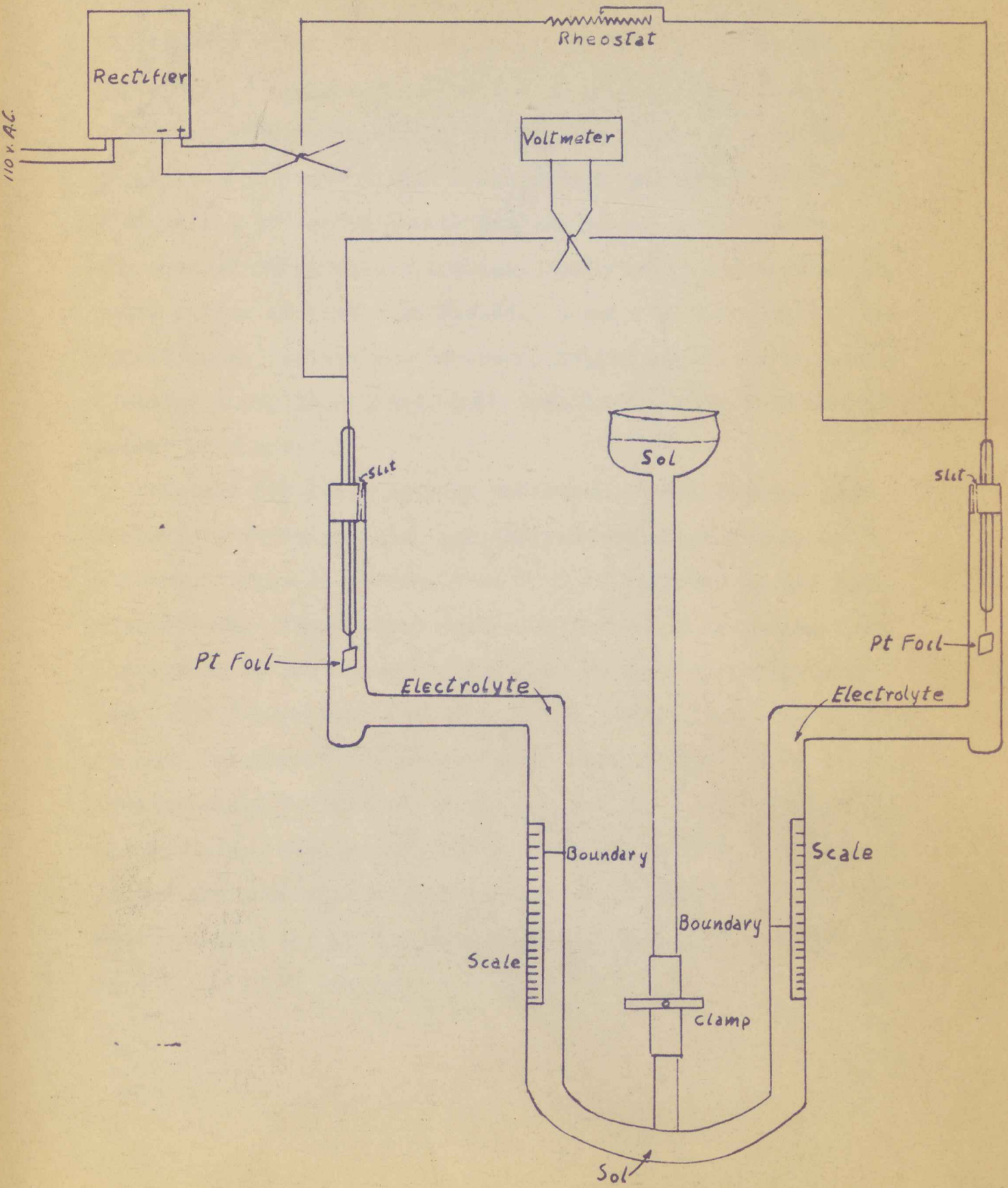
Time	Voltage and Sign of Right Electrode	The Colloidal Surfaces			
		Left		Right	
		Height	Description	Height	Description
3:20	-147 volts	0 mm.	boundary not too sharp	+.5mm.	boundary not very sharp
3:30	-152	-1.5	boundary not very sharp	+ 2	boundary not very sharp
3:45	-152	~ -2	boundary indistinct	+3.5	boundary indistinct
4:05	-148	~ -3	boundary fairly sharp	-	boundary indistinct
4:15	-147	~ -4	boundary sharp	-	boundary indistinct

NOTE: The above data do not bring out this point but it is important to note that the boundary migrations will reverse in direction if the polarity of the electrodes is reversed.

Certain difficulties inherent in electrophoretic measurements are brought out in Table 6. Boundaries sometimes disappear; also multiple boundaries may form due to concentration differences. The electrode reactions may give rise to precipitates and often the sol gels at the boundaries. Some of these difficulties are eliminated by removing the electrodes away from the boundaries as shown in Figure 4; but many other difficulties must still be cleared up before electrophoretic measurements can lead to a quantitative determination of the ζ-potential on some of these sols. The electrophoretic method and charge reversal will be mentioned again in Sections V. and VI. dealing with pH effects.

Figure 4.

Electrophoresis Apparatus



IV. Effect of Silica Concentration on Gelation of "Ludox"

The fact that the precipitation values for electrolytes change with sol concentration has been known for a long time (7); but from the present state of the theory it is still difficult to predict just how the precipitation values of different electrolytes will be affected by changes in concentration of a particular sol. Burton and coworkers (8) state that, in general, with decreasing sol concentration the precipitation values increase for univalent precipitating ions; remain constant for divalent ions; and decrease for trivalent ions. Weiser and others (9,10,11) object to this rule claiming that, in general, such results are only obtained as a matter of chance.

Weiser (9) lists some of the factors that operate most decisively in determining how the precipitation values of different types of electrolytes will be affected by sol concentrations. The smaller number of particles resulting from a decrease in sol concentration require less electrolyte to lower the ζ-potential and bring about coagulation. This factor is most important with electrolytes coagulating in low concentrations. For electrolytes coagulating in high concentrations, Weiser claims that the stabilizing effect of the ion having the same charge as the sol becomes important and the precipitation values for these electrolytes tend to increase upon dilution of the sol.

In studying the effect of silica concentration on the gelation of "Ludox" the electrolytes, potassium chloride and magnesium chloride, are chosen. The procedure involved is simply determining the "limiting values" for these electrolytes on "Ludox" sol at various silica concentrations. The method of determining the "limiting values" is exactly the same as in Section II.

The results are most conveniently represented by the graphical method of Weiser and Nicholas (10) (See Figure 5). Figure 5 shows the way in which the gelling powers of magnesium chloride and potassium chloride vary with the silica concentration in the sol. As abscissa are plotted the concentrations of silica in the sol before mixing. The ordinate values are given as the ratio of the "limiting value" for a particular silica concentration to the "limiting value" when the silica concentration is 30%. In Table 7 these ratios are expressed as: Column 3/Column 2.

Our results as shown in Figure 5 tend to support the views of Weiser. It should prove interesting to press this study a little further by using an electrolyte with a trivalent cation. No such electrolyte was used in the present study because (as is seen from Sections II. and III.) no trivalent cation has been found which gives satisfactory gels under the conditions of this experiment to permit such a study.

When an electrolyte of this type is tested its gelling power will probably be affected in a manner similar to that of magnesium chloride since we have already seen (p. 8) that divalent and trivalent cations possess about the same "limiting values".

Some interesting observations are noted in connection with the gels of low silica content. As the silica concentration decreases, the gels become less stiff and are more apt to synerize. When the silica concentration in the sol is cut down to 5% the gels are quite soft, especially is this so with those formed by magnesium chloride. In fact gelation mixtures containing a low silica concentration which are agitated when on the verge of setting will never set firmly. If the silica concentration in the sol is about 3% or less, precipitation of the silica, rather than gelation, occurs.

Table 7:

Effect of SiO_2 Concentration on Gelation of "Ludox"

KCl

Approx. SiO_2 Concentration in the "Ludox"	Limiting Value in "Ludox" Containing 30% SiO_2	Limiting Value for Sol of Given SiO_2 Conc.	Ratio: Column 3 / Column 2
30%	243 millimols/l.	243 millimols/l.	1.000
25	" "	264	1.086
20	" "	284	1.169
15	" "	308	1.267
10	" "	347	1.428
5	" "	417	1.716

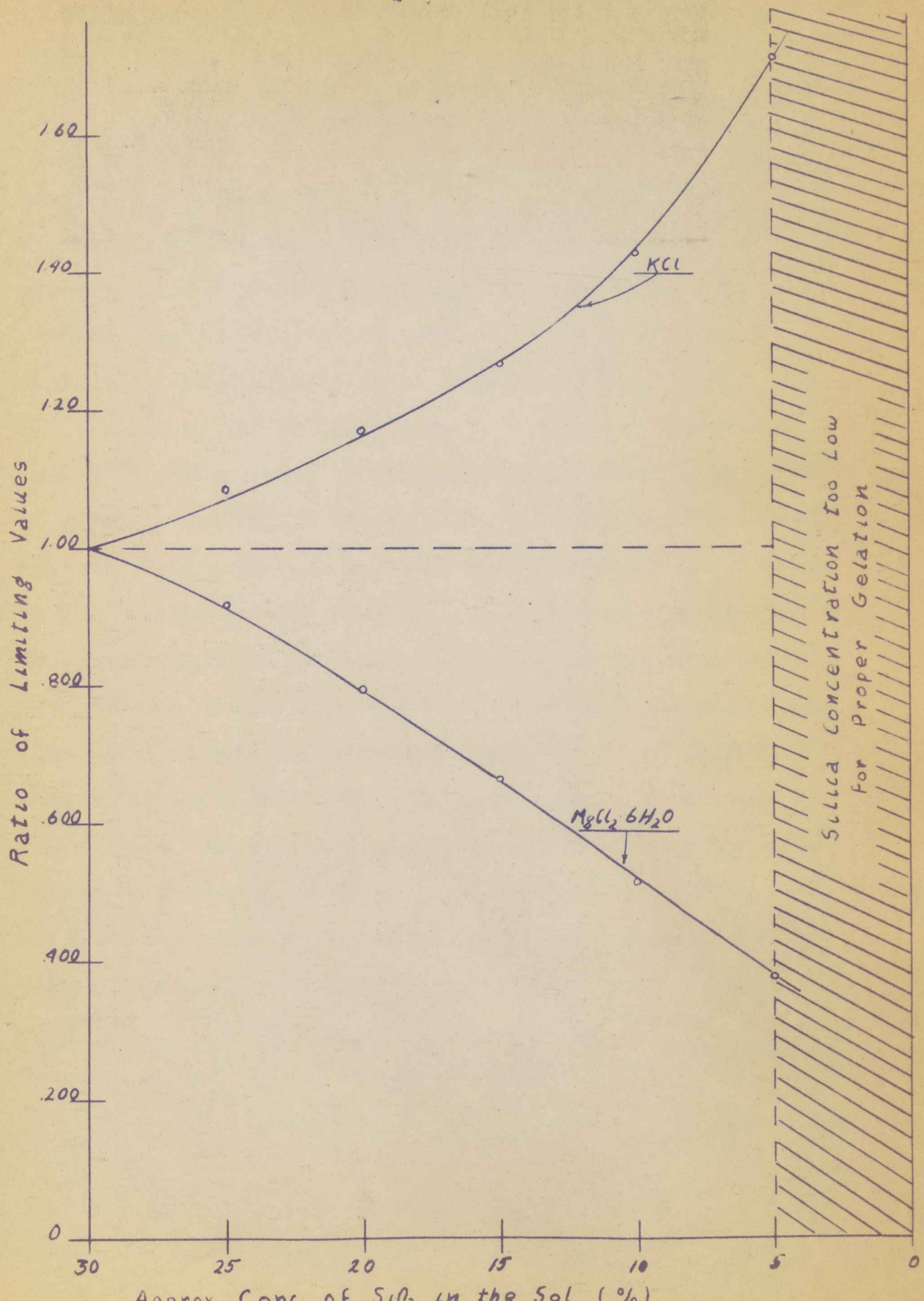
$MgCl_2 \cdot 6H_2O$

Approx. SiO_2 Concentration in the "Ludox"	Limiting Value in "Ludox" Containing 30% SiO_2	Limiting Value for Sol of Given SiO_2 Conc.	Ratio: Column 3 / Column 2
30%	18.5 millimols/l.	18.5 millimols/l.	1.000
25	" "	17.0	.919
20	" "	14.7	.795
15	" "	12.3	.665
10	" "	9.5	.514
5	" "	~7	~.38

NOTE: SiO_2 concentrations given refer to those before mixing. To obtain SiO_2 concentration in the gels divide the figures in Column 1 by two.

Figure 5.

Effect of SiO_2 Concentration



V. pH and its Effects upon the Stability of "Ludox"

A problem of considerable interest in connection with "Ludox" sol has been the study of its behavior as its pH is varied from the normal value of 9.5-10. In particular we are concerned with the stability of the sol itself, its stability toward electrolytes, and the sign of its charge. This section includes a discussion of the stability of the sol and tells something about its charge at various pH values. Section VI. is concerned with the stability of "Ludox" toward electrolytes at these pH values.

The pH of the sol is varied by adding an appropriate amount of concentrated hydrochloric acid or sodium hydroxide to give the desired pH value. The pH of the various sols is measured with a Beckman pH Meter with the exception of those having a value greater than 10. At a pH much greater than 10, the glass electrode is subject to large errors, especially in the presence of sodium ions. For this reason the pH of the more alkaline sols is estimated by the use of an indicator such as Alizarin Yellow-R. The reason that concentrated solutions of the acid and base are used is so that the additions of these solutions to the "Ludox" can be kept small. In this manner the silica concentration in the sol is kept nearly constant, varying by no more than one or two percent.

In Table 8 are listed the stabilities of the sol at the various pH values studied and in Figure 6 these data are represented graphically. Both the original "Ludox" sol with its 30 percent silica and a diluted sol containing 15 percent silica have been studied with respect to stability. The length of time that has been indicated as the stability for these various sols refers to the gelation time of the sol itself with no added electrolyte (except for the acid or base required to bring the sol to the indicated pH). From Figure 6 it is easily seen that with both of the sols studied a minimum in stability is reached at a pH of about 5, the sol with the higher silica concentration being in all cases less stable.

Before trying to explain this variation in the stability of "Ludox", it might be well to mention the results of a few experiments aimed at disclosing the sign of the charge on "Ludox" at various pH values. The classical method for determining the sign of the charge on a sol, electrophoresis, was discussed in detail in Section III.; and this method was also used in an attempt to settle the question of the sign of the charge on "Ludox" over the pH range 1-9. Unfortunately electrophoretic measurements are very difficult to obtain with "Ludox" sol at any pH much below the normal value of 9.5-10.

Table 8:

Effect of pH upon the Stability of "Ludox"

SiO_2 Concentration at Approx. 30%

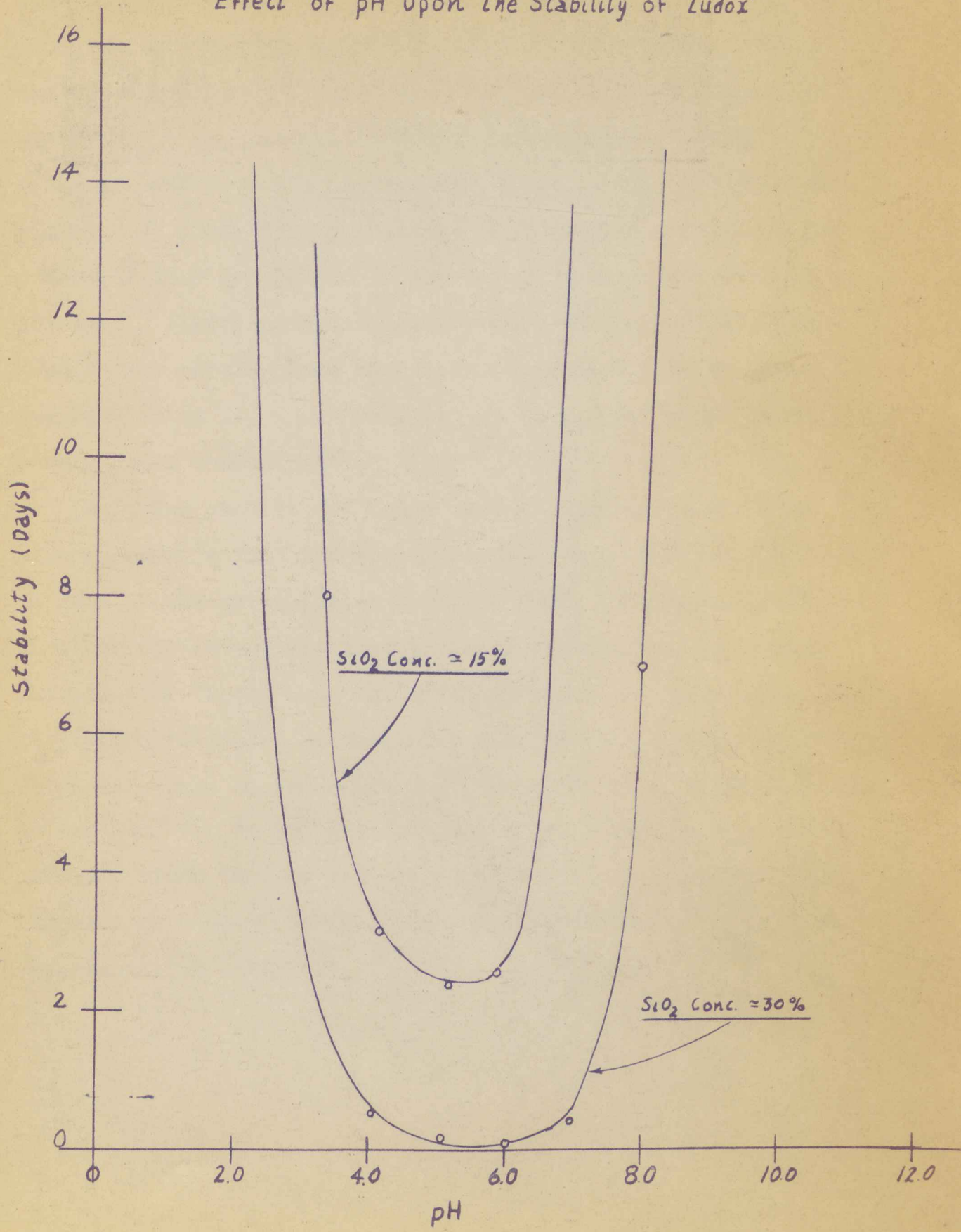
pH of the Sol	Stability
~ 12.5	indefinitely
~ 11.0	"
9.83	"
8.97	"
8.00	7 days
6.98	10 hours
6.00	3 hours
5.05	4 hours
4.03	13 hours
2.04	~ 1 month
1.01	~ 1 month

SiO_2 Concentration at Approx. 15%

pH of the Sol	Stability
9.2	indefinitely
8.2	"
7.17	"
5.87	60-64 hours
5.14	56-58 hours
4.14	75-78 hours
3.34	8 days

Figure 6.

Effect of pH upon the Stability of "Ludox"



Near the point of minimum stability, the sol gels in a very short time inside the electrophoresis apparatus and hence little can be determined by electrophoresis in this range of instability. One run was performed at a pH of 4.90 in which the sol was diluted to increase its stability. Electrophoretic measurements on this sol indicate that the sol is still negative at a pH of 4.90. In the more acid solutions the sol has such a high conductivity (because of the added acid) that the potential drop through it is too low to cause electrophoretic movement. Electrophoretic measurements on a highly-diluted "Ludox" sol should yield much more conclusive results since the highly-diluted sol would be less apt to gel and since it would have a lower conductivity.

Gelation studies on "Ludox" sol in acid media are even less conclusive than the electrophoretic measurements. As will be seen in the next section (Section VI.), high concentrations of electrolytes are required to bring about gelation in acid solutions of "Ludox" and the gelation times are very long. Pairs of electrolytes such as magnesium chloride and potassium sulfate which were used to determine the charge on "Ludox-$Cr(NO_3)_3$" sols in Section III. do not give satisfactory results here as the gelation times for the two electrolytes do not differ sufficiently. (Magnesium chloride causes gelation slightly more rapidly than does potassium sulfate.)

A third observation that throws some light upon the sign of the charge on "Ludox" sol in acid solutions is the fact that gelatin and "Ludox" are mutually precipitated in acid solutions. (The particular experiment referred to here was performed at a pH of 3.42). Since gelatin has a positive charge on the acid side of its isoelectric point (4.7), this experiment also tends to show that "Ludox" is charged negatively even in acid media.

The reader will undoubtedly conclude at this point that our information as to the charge on "Ludox" at low pH values is rather inconclusive and he is correct in so doing; for this, the determination of the sign of the charge and of the magnitude of the ζ-potential of "Ludox" at various pH values, is one of the major problems yet to be solved.

Coming back to the question of why the stability of the sol varies as it does with respect to pH we can only offer this tentative explanation:

"Ludox" sol at a pH of about 10 consists of hydrated silica particles containing a sufficient number of surface hydroxyl ions to give the sol a negative charge. As an acid, such as HCl, is added to the sol, there is a tendency for hydrogen ions to be strongly adsorbed; and in this process of adsorption the hydrogen ions combine with the surface hydroxyl ions to form water. This much of the hypothesis is reasonable because it is observed experimentally that only a small fraction of the acid added affects the pH meter (see Appendix I. for an approximate calculation).

This means that most of the added hydrogen ions are within the double layers of the micelles in which case the combination with hydroxyl ions could proceed as just mentioned.

This combination of hydrogen and hydroxyl ions to form water tends to leave the particles with only a very small charge and hence the sol becomes unstable. This then explains the instability of the sol over the pH range 4-8. But with increasing acidity we notice that the sol becomes more stable (see Figure 6). This would indicate that the charge on the micelles is building up again and from the discussion on the preceding pages we think that this charge is negative. Now it is hard to say just what is stabilizing the sol. Perhaps we may compare this to the increase in the ζ-potential of glass particles upon the addition of very small amounts of potassium chloride (12). If there is any appreciable amount of chloride ion stabilizing the sol, it might be possible to determine this potentiometrically in the manner described by Weiser (13).

At any rate whenever further data are compiled on the sign of the charge, on the ζ-potential, and on the distribution of ions within the double layers of the micelles, one may be able to actually propose a structure for the micelles throughout the whole pH range just as we have done in Figure 1a. for "Ludox" at a pH of 9.5-10.

VI. Effect of pH on the Gelation of "Ludox" by Electrolytes

In the preceding section we considered the stability of the "Ludox" sol itself throughout a wide pH range and here we shall extend our discussion of pH to show how the gelling powers of various electrolytes vary with pH. The method of adjusting and measuring the pH of the various sols as given on page 27 is followed in this section also. Because of hydrolysis many of the electrolytes studied have, in their aqueous solutions, a pH far removed from the neutral 7. For this reason the pH values in which we are particularly interested in this section are those existing after the sol and electrolytes are mixed.

A word about the actual procedure may be in order here. After adjusting the sol to a given pH value, 5.00 ml. of the sol are transferred to a small beaker. Now 5.00 ml. of a particular electrolyte solution are added, the solutions are mixed well, and the pH is recorded. The gelation mixture is transferred to a test tube and the time required for gelation is observed.

Table 9 consists of a compilation of gelation data for the various electrolytes studied over a wide pH range. These data are represented in graphical form in Figure 7 where the gelation time is plotted against the pH of the mixtures. The concentrations of the various electrolytes appearing on this graph refer to concentrations after mixing.

Table 9:

Effect of pH on the Gelation of "Ludox" by Electrolytes

A. KCl

Concentration of KCl in Final Mixture	pH of the Original Sol	pH of the Final Mixture	Time of Gelation
243 millimols/l.	~12.5	~12.4	6 hr.
"	~11.0	~10.4	2 hr. 10 min.
"	9.83	9.27	1 hr. 5 min.
"	9.00	8.53	35 min.
"	8.01	7.70	20 - 25 min.
"	6.96	6.68	30 min.
"	5.76	5.50	2 hr. 40 min.
"	5.01	4.88	9 hr.
"	3.98	3.97	30 - 31 hr.
"	3.00	3.29	3 - 4 days
"	2.04	----	no gelation
"	1.01	1.31	no gelation

Concentration of SiO_2 in the gelation mixtures $\simeq$ 15%

Temperature = 25±4°C

Table 9: (Cont'd)

Effect of pH on the Gelation of "Ludox" by Electrolytes

B. K_2SO_4

Concentration of K_2SO_4 in Final Mixture	pH of the Original Sol	pH of the Final Mixture	Time of Gelation
169 millimols/l.	~12.5	~12.4	7 - 8 hr.
"	~11.0	~10.4	2 hr.
"	9.83	9.23	1 hr.
"	9.00	8.53	27 min.
"	8.01	7.70	22 min.
"	6.96	6.69	35 min.
"	5.76	5.50	3 hr. 15 min.
"	5.01	4.93	11 - 12 hr.
"	3.98	4.14	38 hr.
"	3.00	3.71	3 days
"	2.04	----	no gelation
"	1.01	1.70	no gelation

Concentration of SiO_2 in the gelation mixtures $\simeq$ 15%

Temperature = 25±4°C

Table 9: (Cont'd)

Effect of pH on the Gelation of "Ludox" by Electrolytes

C. $AlCl_3 \cdot 6H_2O$

Concentration of $AlCl_3 \cdot 6H_2O$ in Final Mixture	pH of the Original Sol	pH of the Final Mixture	Time of Gelation
20.0 millimols/l.	~12.5	9.1	wht. ppt. immd. gel
"	~11.0	6.30	" " " "
"	9.83	5.5	" " " "
"	9.00	3.88	" " " "
"	8.01	3.55	" " " "
"	6.96	3.35	wht. ppt. 10 min.
"	5.76	3.10	1 - 2 days
"	5.01	2.94	10 - 12 days
"	3.98	2.92	no gelation
"	3.01	2.80	" "
"	2.04	----	" "
"	1.01	1.30	" "

Concentration of SiO_2 in the gelation mixtures ≃ 15%

Temperature = 25±4°C

Table 9: (Cont'd)

Effect of pH on the Gelation of "Ludox" by Electrolytes

D. $MgCl_2 \cdot 6H_2O$

Concentration of $MgCl_2 \cdot 6H_2O$ in Final Mixture	pH of the Original Sol	pH of the Final Mixture	Time of Gelation
50.0 millimols/l.	9.83	8.50	wht. ppt. immd. gel
"	9.00	8.12	" " " "
"	8.01	7.57	50 min.
"	6.96	6.70	5 hr.
"	5.76	5.57	12 - 14 hr.
"	5.01	5.09	20 - 22 hr.
"	3.98	4.15	56 - 57 hr.
"	3.00	3.34	6 days

E. $Cr(NO_3)_3 \cdot 9H_2O$

Concentration of $Cr(NO_3)_3 \cdot 9H_2O$ in Final Mixture	pH of the Original Sol	pH of the Final Mixture	Time of Gelation
24.3 millimols/l.	~12.5	8.60	no gelation
"	~11.0	6.33	12 hr.
"	9.83	5.45	1 hr. 5 min.
"	9.00	5.13	no gelation
	⋮	⋮	⋮
"	1.01	----	no gelation

Figure 7.

Effect of pH on Gelation by Electrolytes

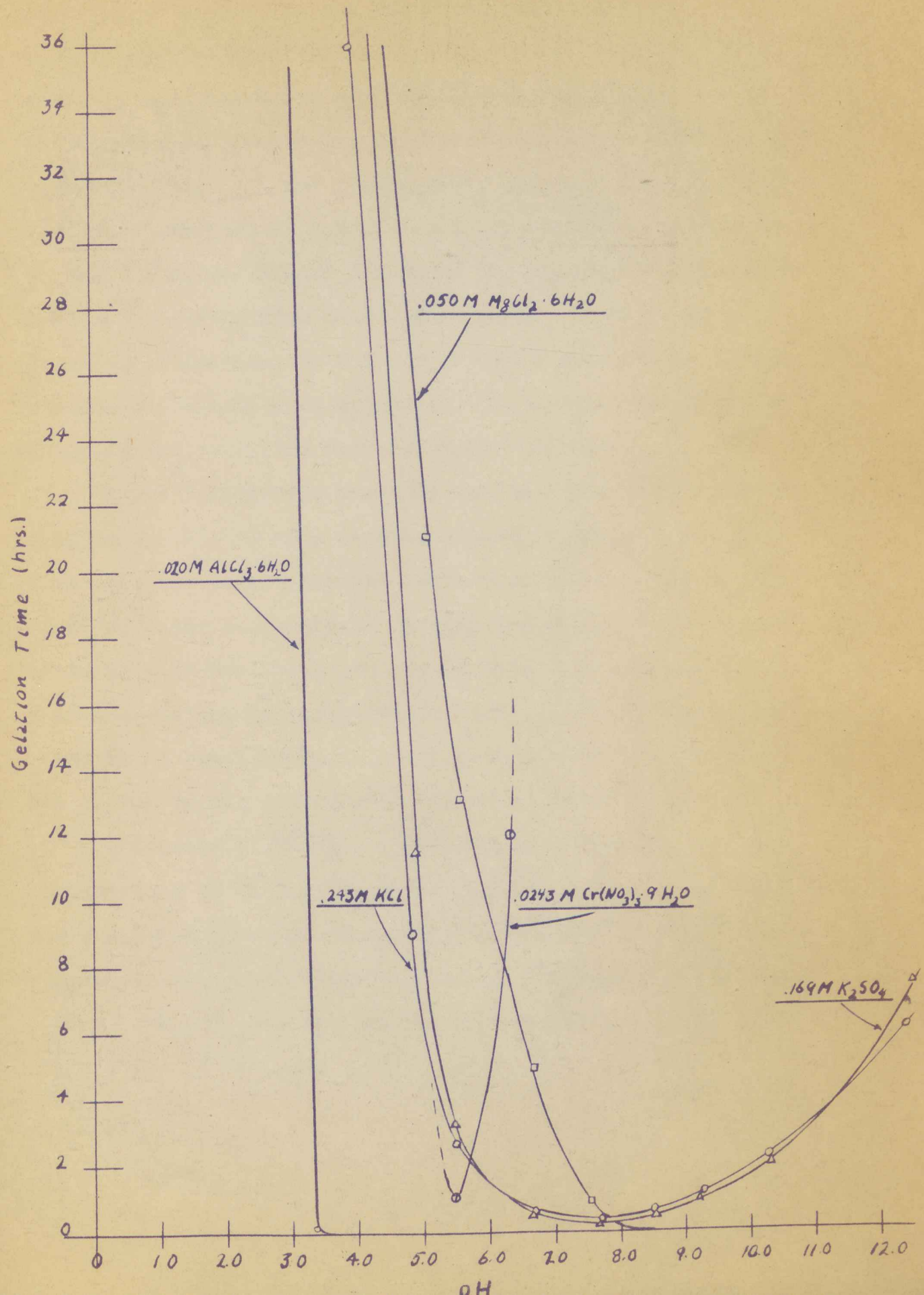


Figure 7 supplies us with a considerable amount of information concerning the effect of electrolytes at various pH values. The electrolytes, potassium chloride and potassium sulfate, are seen to be very similar in their effects over the whole pH range studied and we may consider them together. By referring back to Table 3 the reader will see that the particular concentrations of each of these two electrolytes correspond to the "limiting values" discussed in Section II. i.e. these are the concentrations that are required to bring about gelation in one hour at the normal pH of about 9.8. Because the concentrations were so chosen, the curves for potassium chloride and potassium sulfate nearly coincide.

Figure 7 indicates that the gelling power for a univalent ion, such a K^+, is at a maximum between a pH of 7 and 8; and that once the pH of the mixture is much below 5, the gelling power of these electrolytes is very low, gelation being achieved only over long periods of time. In Figure 6 we saw that the minimum in stability for the sol falls between pH 5 and 6. A question that immediately arises is why don't the minima in the two curves come at the same pH.

In Section V. we made the assumption that the decrease in stability of "Ludox" near the neutral point is caused by the formation of water on the surface of the silica particles with a consequent decrease in charge, a minimum in charge at a pH of about 5 causing a minimum in stability at this point.

The addition of an electrolyte to "Ludox" at this pH might require first the building up of a charge on the micelles by one of the ions and then gelation by the other. This would require a rather high concentration of electrolyte or in other words a fairly long gelation time. At the pH of 7 or 8 the charge on the micelles is low, though not at a minimum. But here the added electrolyte would act directly to cause gelation without first putting any additional charge on the micelles, hence the gelling power would be greatest in this case. Below pH 5 the structure of the silica micelles is such that gelation is very hard to achieve.

The salts of magnesium and aluminum present a more complicated picture. Aluminum hydroxide tends to precipitate out readily over a large portion of the pH range studied and many of the gels formed by the addition of aluminum chloride to "Ludox" are probably co-gels of silica and aluminum hydroxide. However when the pH of "Ludox"-$AlCl_3$" mixtures is lowered toward a value of 3, a great stability is noticed, gelation being very hard to achieve below this point. Magnesium chloride behaves in a somewhat similar manner except that with this electrolyte magnesium hydroxide is precipitated out only at pH values above 8. Below pH 8 the magnesium chloride is very much like the potassium salts studied in that gelation becomes much harder to achieve with increasing acidity.

The experiments conducted in this section with chromium nitrate present a possible correlation between pH effects and the "irregular-series" studied in Section III. From Figure 7 it is seen that a concentration of chromium nitrate in the gelation mixtures of .0243 M can only cause gelation if the pH is between 5.1 and 6.5. This fact suggests two possible relationships between pH and "irregular-series" with chromium.

One possibility is that the pH of the gelation mixture is the sole factor which determines gelation by chromium nitrate i.e. the pH of the gelation mixture would have to fall in this range in order for gelation to occur. Table 10 lists the results of an experiment which was performed to test this point. It is seen from the table that those concentrations of chromium nitrate which cause gelation (cf. Figure 2) also yield a gelation mixture whose pH falls in the range 5.1-6.5.

Higher concentrations of chromium nitrate cause a lower pH, no gelation, and as we saw in Section III. a charge reversal. Lower concentrations of chromium nitrate when mixed with "Ludox" have a pH>6.5 and produce no gelation. Thus it is seen from Table 10 that only those solutions whose pH lie between 5.1 and 6.5 cause gelation. And from Table 4 and Figure 2 only those solutions having a concentration in the gelation mixture in the range .0175M to .027M cause gelation. In short the two gelation ranges pH 5.1-6.5 and concentration .0175M to .027M coincide.

Table 10:

Effect of pH on Gelation by $Cr(NO_3)_3 \cdot 9H_2O$

Concentration of $Cr(NO_3)_3 \cdot 9H_2O$ in Final Mixture	pH of the Original Sol	pH of the Final Mixture	Time of Gelation
50.0 millimols/l.	9.83	4.78	no gelation
29.4	"	5.02	no gelation
26.4	"	5.16	4 days
22.7	"	5.38	1 hr. 15 min.
20.0	"	5.89	4 - 6 hr.
16.7	"	6.95	no gelation

The other possibility is that some of the solutions in Table 10 which fail to cause gelation would do so if the gelation mixtures could be buffered over a series of pH values. This suggests that the gelation and charge reversal by chromium nitrate may depend not just upon concentration or pH alone but upon some function of the two of them.

This may be possible for according to a statement by Weiser (14): "As already noted, the reversal in the sign of charge is brought about by strong adsorption either of an ion or of a hydrous oxide in the case of salts with multivalent cations that may hydrolyze appreciably." Applying this to our case it might possibly be that a certain ratio of Cr^{+++}/Cr_2O_3 is required to cause either gelation or charge reversal. The concentration of Cr_2O_3 would depend in turn both on the concentration of Cr^{+++} and on the pH and hence a relationship is suggested between the concentration of chromium nitrate, the pH, and "irregular-series". Future studies on the effects of chromium nitrate in buffered "Ludox" sols should yield some useful information to explain this peculiar relationship.

VII. Gelation and Dehydration by Ethyl Alcohol

Ethyl alcohol possesses the ability to gel "Ludox" or to dehydrate it with the subsequent precipitation of the silica contained in the sol. The phenomenon that is observed in any particular case depends upon the relative amounts of alcohol and "Ludox" present. If the concentrations of ethyl alcohol and silica are such as shown in Figure 8, then the gelation curves are like those pictured. One point that is brought out by these curves is the fact that the greater the number of sol particles (i.e. the higher the silica concentration) the more readily the sol is gelled by ethyl alcohol. (See Appendix II. for a discussion of the calculation of the silica concentrations appearing in Figure 8).

The data of Figure 8 suggest the possibility of treating the three component system: SiO_2-H_2O-C_2H_5OH on a triangular phase diagram. By working with mixtures falling over the entire area of this diagram, interesting relationships should arise which will indicate the regions of gelation and those of precipitation. This is, in our estimation, a point which should prove very promising for future workers.

The dehydration of the silica particles in "Ludox" by ethyl alcohol is a very interesting process for it has been shown to be reversible. The principal condition necessary for the precipitation of silica rather than gelation of the sol is that the alcohol must be present in a large excess. Precipitation and repeptization of silica by ethyl alcohol may be brought about in the following manner:

A small volume of "Ludox" (about 20 ml.) is added to a large excess of ethyl alcohol (about 150 ml.) and the precipitated silica is filtered off by suction. The precipitate is then repeptized by adding approximately 80 ml. of a very dilute solution of sodium hydroxide and mixing for 45 minutes with a mechanical stirrer. The sol is then filtered off from the slight amount of unpeptized silica and placed in a collodion bag for evaporation, being allowed to evaporate to a volume of approximately 25 ml.

Table 11 lists data which illustrate the reversibility of this precipitation of silica. What we have done here is to simply dilute 20 ml. of the original "Ludox" up to 25 ml. and to compare this sol with the repeptized one described above. Since these two sols are so similar it appears that the action of ethyl alcohol is merely the removal of water from the silica particles without any alteration of the double layers. Repeptization puts back the water removed, and by having the same constitution as the original "Ludox", the repeptized sol behaves very similarly.

Figure 8.

Gelation by Ethyl Alcohol

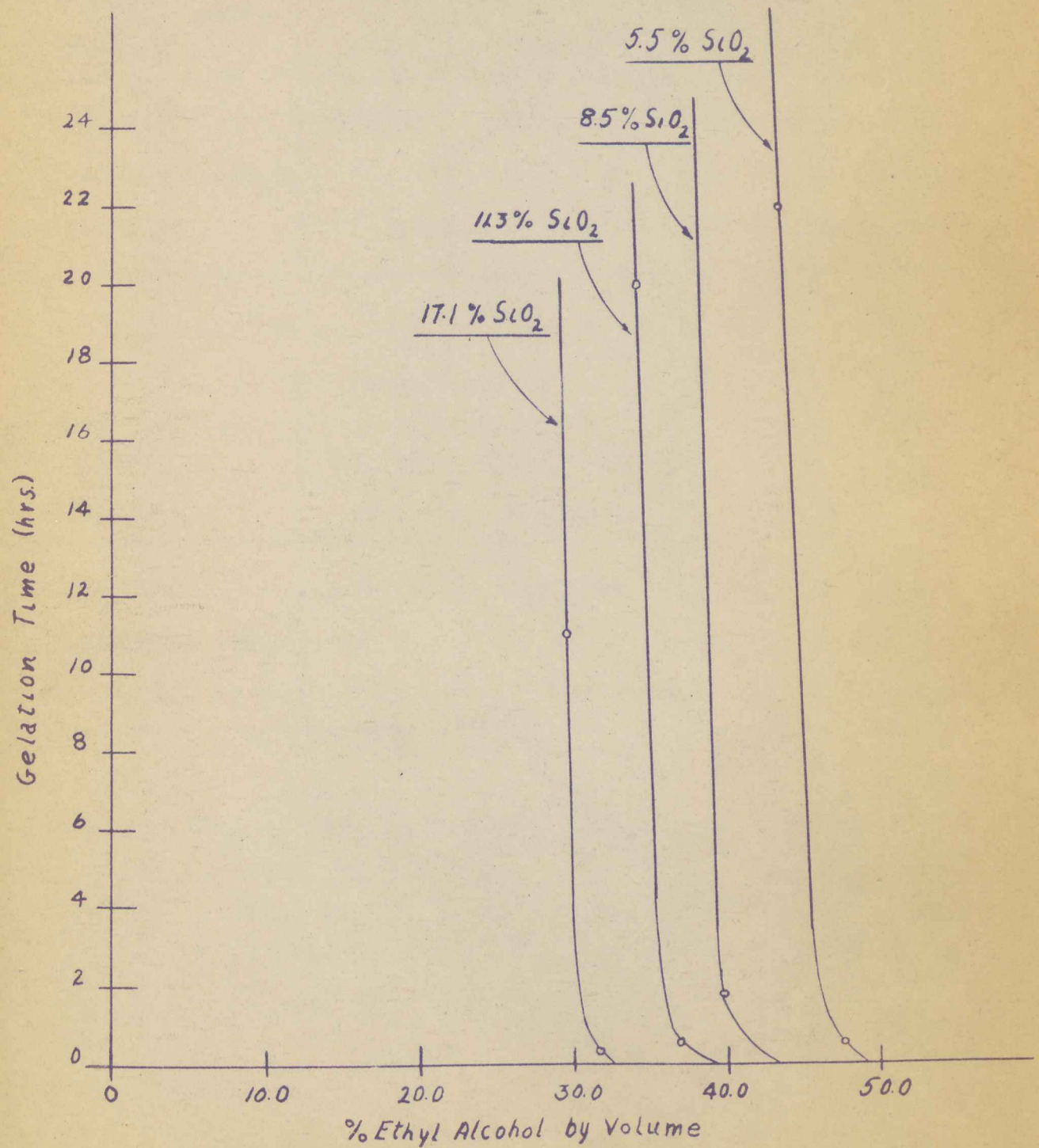


Table 11:

Comparison of Original and Repeptized Sols

Original Sol

Added Component	Vol. of Sol	Vol. of Added Component	Results
1.00M KCl	5.00 ml	5.00 ml	Gelation: 2-3 min.
.040M $MgCl_2 \cdot 6H_2O$	"	"	Gelation: 30 sec.
95% EtOH	"	"	Immd., soft, white gel

Repeptized Sol

Added Component	Vol. of Sol	Vol. of Added Component	Results
1.00M KCl	5.00 ml	5.00 ml	Gelation: 3 min.
.040M $MgCl_2 \cdot 6H_2O$	"	"	Gelation: 1 min.
95% EtOH	"	"	Immd., soft, white, gel

Concentration of SiO_2 in the Sols $\simeq$ 24%

VIII. Effect of non-Electrolytes

The effect of non-electrolytes on hydrophobic sols is not always an easy matter to explain. Either sensitization or stabilization can be observed depending upon the particular sols and non-electrolytes being studied. Weiser and Mack (15) list some of the most important factors in determining the effect of non-electrolytes. They are the effect 1) on the dielectric constant of the medium 2) on the viscosity of the sol 3) on the degree of ionization of any electrolytes present and 4) on the selective adsorption of stabilizing ions and precipitating ions by the sol particles.

In studying the effect of non-electrolytes on "Ludox" we have not checked, specifically, any of the factors cited above; but we have formulated a hypothesis based on the adsorption of non-electrolytes on the sol particles and certain of the factors mentioned by Weiser and Mack may be inherently operating in conjunction with this adsorption process. Our hypothesis for the effect of non-electrolytes on "Ludox" states essentially that non-electrolytes tend to be adsorbed with their hydrophilic groups toward the silica particles.

In other words the silica particles are hydrophilic in the sense that they are hydrated, and when a non-electrolyte is added to the sol, the hydrophilic portions of the molecules are held by the hydrophilic (i.e. hydrated) centers of the silica particles.

If the parts of the non-electrolyte molecules which are turned away from the silica particles also have hydrophilic groups attached, then the particles take on an even greater hydrophilic nature and stabilization results. If hydrophobic portions of the non-electrolyte molecules are exposed, the sol becomes more hydrophobic and is thus sensitized.

So far we have only mentioned sensitization and stabilization of "Ludox" by non-electrolytes without stating how these phenomena are detected. When we speak of sensitization or stabilization of "Ludox" by non-electrolytes, we mean sensitization or stabilization toward electrolytes, in particular in the determinations of this section toward potassium chloride. The fourth factor stated on the preceding page might apply differently for ions of different valence types and it should be interesting in future studies to see if those non-electrolytes which sensitize or stabilize with respect to potassium chloride also do so toward electrolytes of other valence types.

The procedure followed in studying the effects of non-electrolytes is to prepare a modified sol by mixing an equal volume of "Ludox" and the non-electrolyte being studied. To five milliliters of these modified sols are added five milliliters of potassium chloride solutions of various concentrations and the gelation times are recorded.

From these data it is possible to plot curves such as those appearing in Figures 9 and 10. If a run is made in which pure water is substituted for the non-electrolyte, a standard curve is obtained (see Figures 9 and 10). Now any non-electrolyte yielding a gelation curve falling below the standard curve causes sensitization; one whose gelation curve is above the standard curve stabilizes the "Ludox".

Figure 9 contains gelation curves for non-electrolytes exhibiting stabilization and Figure 10 for those which sensitize "Ludox". It might be well at this point to list some of the conditions existing for the various determinations of this section. They are:

1.) Conc. of SiO_2 in the gels $\simeq 7.5\%$

2.) Conc. of non-electrolyte in the gels = as indicated in the respective graphs

3.) Conc. of KCl in the gels = abscissa values on the graphs

4.) Temperature = $25 \pm 4^{\circ}C$

The data from which the individual curves are derived are given in condensed form in Tables 12 and 13. In addition we have included Figures 11 and 12 which are representations of the orientation of the adsorbed non-electrolytes on the silica particles. For the remainder of this section we shall give a brief account of the effect of each of the non-electrolytes studied and try to explain these effects on the basis of the adsorption hypothesis postulated on page 49.

Table 12:

Effect of non-Electrolytes - Stabilization

Conc. of KCl in Final Mixture (millimols/l.)	Gelation Time when the Indicated non-Electrolyte is Present		
	a) Glycerol 25% (Vol)	b) .5M Sucrose	c).5M Glucose
500	5 min.	6 min.	7 min.
417	15 min.	16 min.	18-20 min.
357	35-40 min.	40-42 min.	50-52 min.
313	1 hr. 30 min.	1 hr. 30 min.	~2 hr.
278	4-4½ hr.	~4 hr.	~5 hr.

Conc. of KCl in Final Mixture (millimols/l.)	Gelation Time when the Indicated non-Electrolyte is Present		
	d) 2.5M Urea	e) .25M Thiourea	f) Standard (H_2O)
500	10-12 min.	3-4 min.	3-4 min.
417	40 min.	15-16 min.	10 min.
357	2-2½ hr.	40-45 min.	32 min.
313	6-6½ hr.	1 hr. 45 min.	1 hr. 10 min.
278	12-14 hr.	4-5 hr.	4 hr.

Concentration of SiO_2 in the gels $\simeq$ 7.5%

Table 13:

Effect of non-Electrolytes - Sensitization

Conc. of KCl in Final Mixture (millimols/l.)	Gelation Time when the Indicated non-Electrolyte is Present		
	a) 12.5% Ethyl Alcohol	b) 25% Ethylene Glycol	c) 2.5M Acetamide
500	inst. gelation	½-1 min.	inst. gelation
417	" "	2 min.	1 min.
357	" "	6-8 min.	3 min.
313	" "	20 min.	10-12 min.
278	" "	50 min.	30 min.

Conc. of KCl in Final Mixture (millimols/l.)	Gelation Time when the Indicated non-Electrolyte is Present		
	d) 12.5% Triethanolamine	e) .025M Sodium oleate	f) Standard (H_2O)
500	inst. gelation	3 min.	3-4 min.
417	1 min	10 min.	10 min.
357	5 min.	25-30 min.	32 min.
313	15 min.	65-70 min.	1hr-10 min.
278	45 min.	2 hr 40 min.	3 hr.

Concentration of SiO_2 in the gels $\simeq$ 7.5%

Figure 9.

Effect of non-Electrolytes — Stabilization

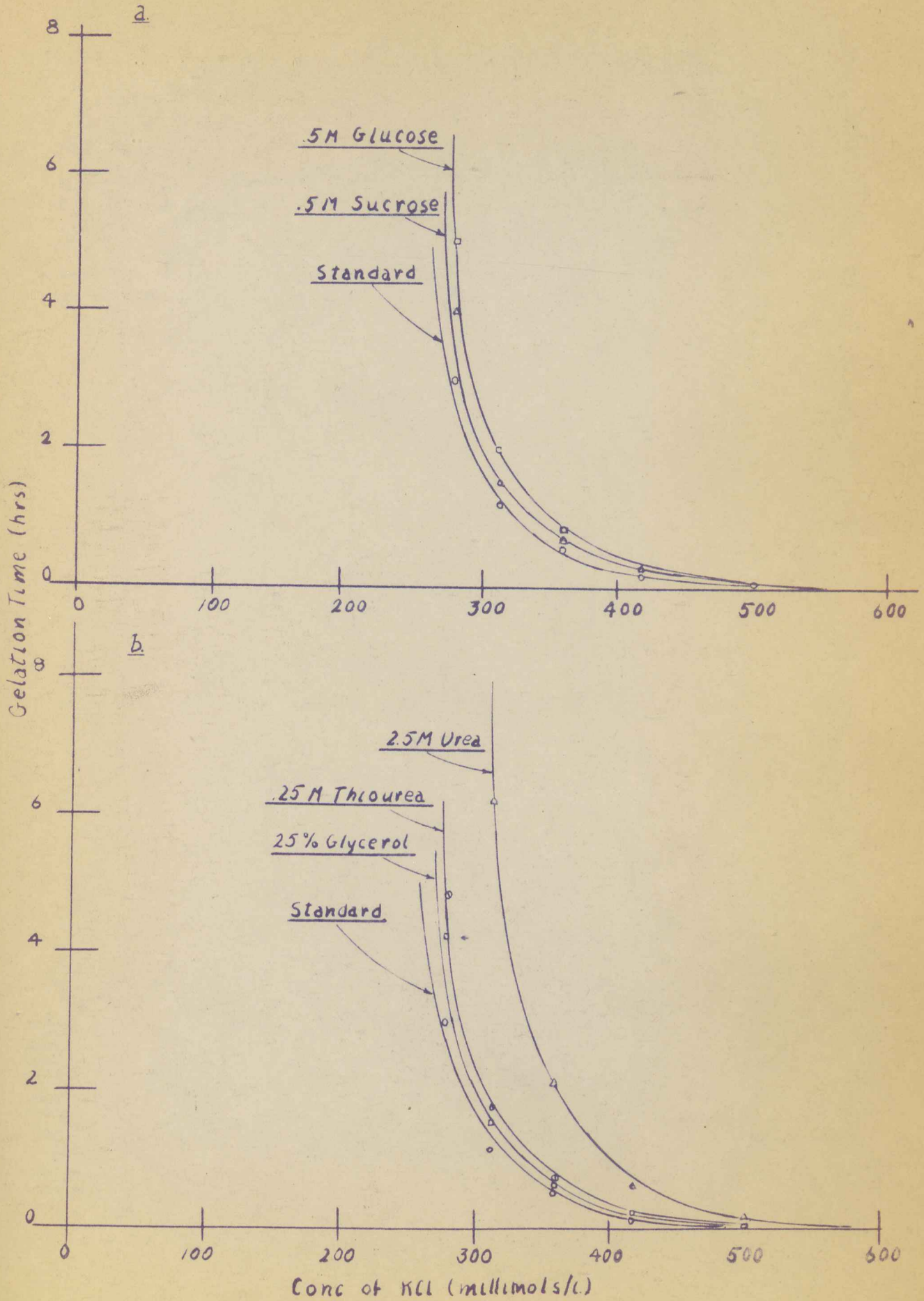
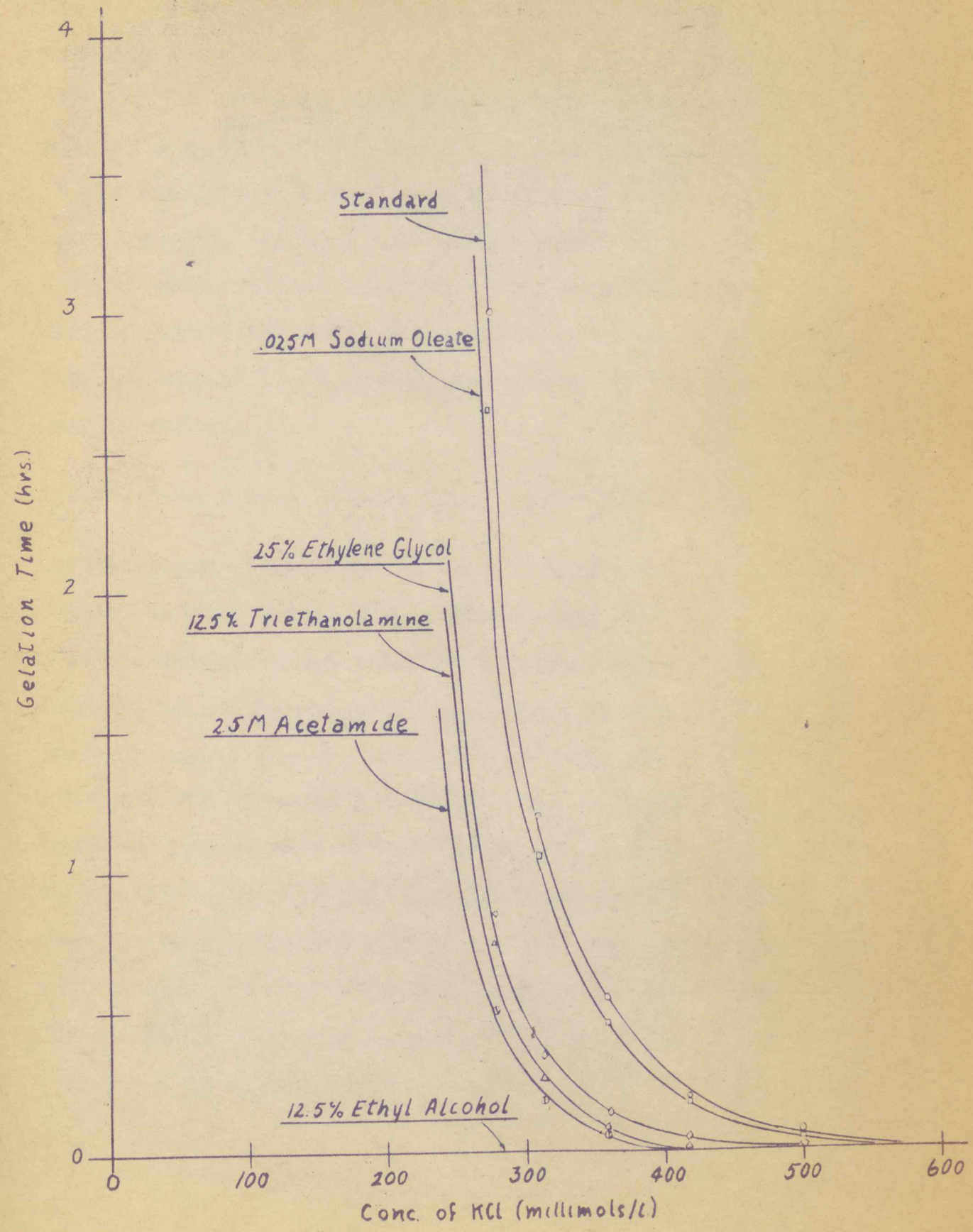


Figure 10.

Effect of non-Electrolytes — Sensitization



1.) Ethyl alcohol (Table 13a, Figures 10 and 12a.):

We have already studied some of the effects of ethyl alcohol in Section VII; but here we are interested in studying the effects of low concentrations of ethyl alcohol on "Ludox". Although ethyl alcohol in low concentrations neither gels the "Ludox" nor precipitates the silica from it, it sensitizes "Ludox" very greatly as far as electrolytes are concerned. In this case we can postulate that the ethyl alcohol molecules are adsorbed on the micelles in such a way that the hydrophilic-OH groups are held to the particles with the hydrophobic CH_3CH_2-groups projecting out into the dispersion medium.

2.) Ethylene glycol (Table 13b, Figures 10 and 12b.):

Ethylene glycol is also seen to sensitize "Ludox" sol but not so strongly as does ethyl alcohol itself. In this case sensitization may occur by the adsorption of the two hydrophilic -OH groups with the subsequent turning out of the hydrophobic $\overset{|}{C}H_2\text{-}\overset{|}{C}H_2$ unit into the intermicellar liquid. Due to steric factors, however, it is conceivable that ethylene glycol could be adsorbed in the manner: $\overset{OH}{\overset{|}{C}}H_2\text{-}\overset{OH}{\overset{|}{C}}H_2$. Undoubtedly both of these configurations about the silica micelles occur, but the hydrophobic external grouping is predominate. Nevertheless some hydrophilic groups must be exposed since sensitization with ethylene glycol is not so pronounced as with ethyl alcohol.

3.) Glycerol (Table 12a, Figures 9b and 11a):

In glycerol we have come to a molecule with three -OH groups. Here steric factors are such that all three -OH groups are not necessarily on the same side of the carbon chain. As a result one or two -OH groups may be adsorbed but there are always a number of -OH groups projecting outward from the silica particles. This increases the hydrophilic nature of the sol and hence in the presence of glycerol a slight stabilization of "Ludox" toward potassium chloride results.

4.) Sucrose (Table 12b, Figure 9a):

Sucrose is a polyhydroxy compound and hence the adsorption of sucrose on silica particles would always leave some -OH groups tending to make the sol more hydrophilic. Sucrose, like glycerol then, exhibits a slight stabilizing tendency in its effects on "Ludox".

5.) Glucose (Table 12c, Figures 9a, and 11b):

Glucose is also a polyhydroxy compound and probably functions similarly to the sucrose. With glucose, however, a slightly stronger stabilizing effect is noted.

6.) Urea (Table 12d, Figures 9b and 11c.):

Urea exhibits a marked stabilizing effect on "Ludox" but this is entirely in line with our adsorption hypothesis; for structurally urea is a very hydrophilic substance: $O=C\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}$. It would not be possible for all three of these groups to be adsorbed simultaneously by the silica particles with the result that some hydrophilic centers, either the $>C=O$ or the $-NH_2$ groups, are left projecting out into the dispersion medium to stabilize the sol.

7.) Thiourea (Table 12e, Figures 9b. and 11d.):

Thiourea also stabilizes "Ludox" but not so strongly as does urea. Structurally thiourea differs from urea in that it possesses a $>C=S$ group in place of the $>C=O$ of the urea. We can probably say that the lessening of the stabilizing effect with thiourea is due to the large number of the relatively less hydrophilic $>C=S$ groups that are turned outward into the intermicellar liquid. Also the fact that the urea and thiourea differ in concentration by a factor of ten may account for some of the difference existing between them.

8.) Acetamide (Table 13c, Figures 10 and 12c.)

In acetamide we have the structure: $O=C\begin{smallmatrix}NH_2\\CH_3\end{smallmatrix}$. The majority of the adsorbed non-electrolyte molecules probably attach themselves to the silica particles by their two hydrophilic groups leaving hydrophobic $-CH_3$ groups unadsorbed. This manner of adsorption accounts for the sensitization observed with acetamide.

9.) Triethanolamine (Table 13d, Figures 10 and 12d.):

In studying triethanolamine we can imagine the molecule to be somewhat tetrahedral in shape with the -OH groups forming three of the vertices and the tertiary nitrogen the fourth. Adsorption of a molecule of triethanolamine on a silica particle probably takes place with the hydroxyl groups being adsorbed and the three ethyl chains and the tertiary nitrogen projecting into the dispersion medium. The net character of three ethyl chains and a tertiary nitrogen is probably hydrophobic and hence sensitization of the "Ludox" is noticed.

10.) Monoethanolamine:

Structurally monoethanolamine ($H_2NCH_2CH_2OH$) is very similar to ethylene glycol and we should expect a sensitization of "Ludox" by the monoethanolamine. Although upon mixing pure ethanolamine and "Ludox" a gel is formed, when the concentration of the amine is lowered no gelation occurs; and, in fact, the sol becomes very stable toward KCl. More non-electrolytes of the monoethanolamine type must be studied before the adsorption hypothesis can be accepted in full.

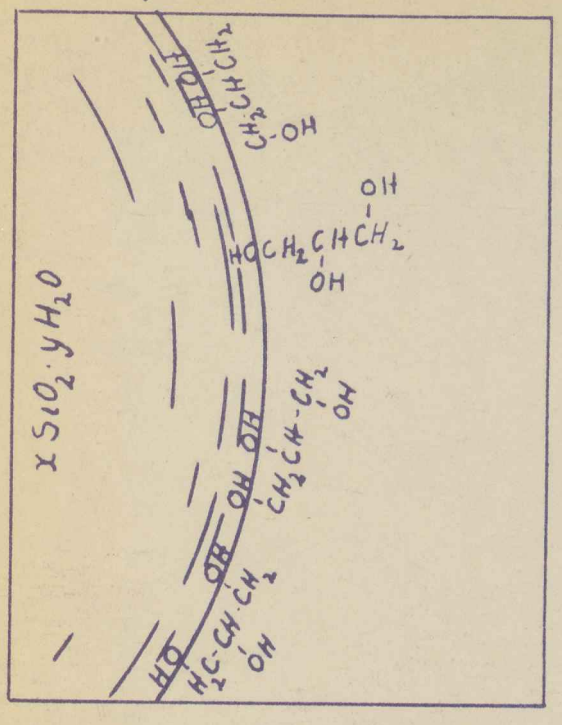
11.) Sodium Oleate (Table 13e, Figure 10):

Sodium oleate was included in these studies to see if changes in surface and interfacial tensions upon the addition of non-electrolytes to "Ludox" might not be responsible for the phenomena noted. Sodium oleate appears to have no effect in either stabilizing or sensitizing "Ludox". The slight sensitization suggested in Figure 10 could be due merely to the presence of additional electrolyte (i.e. the sodium oleate).

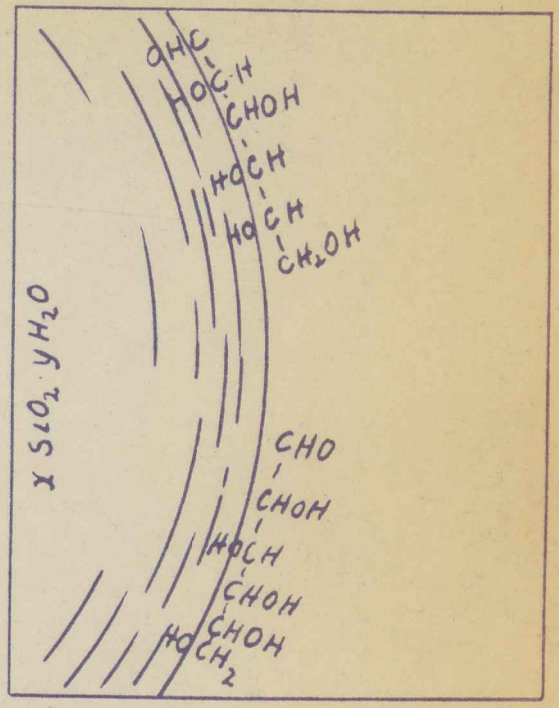
Figure 11.

Effect of non-Electrolytes — Stabilization

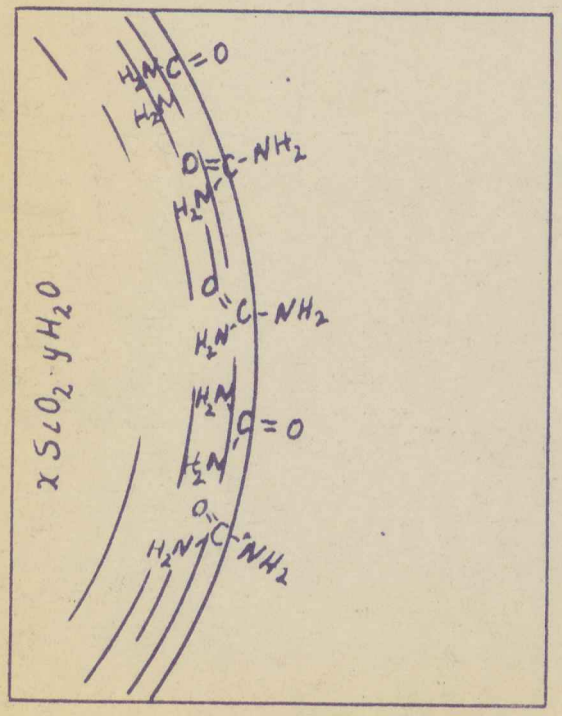
a. Glycerol



b. Glucose



c. Urea



d. Thiourea

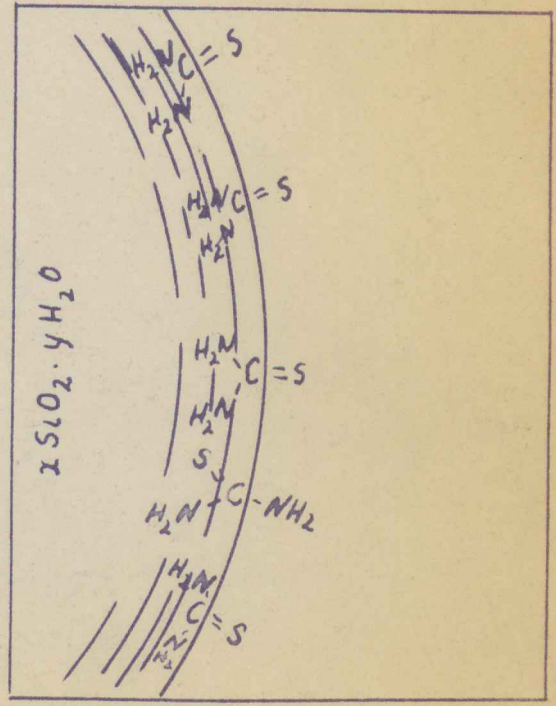
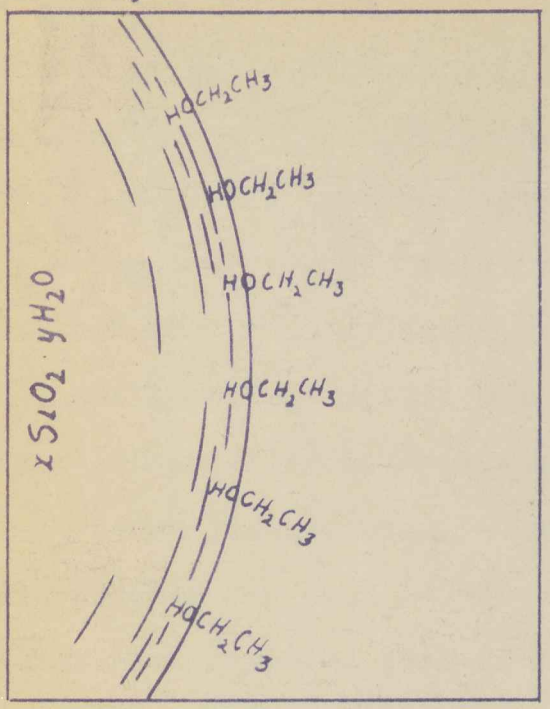


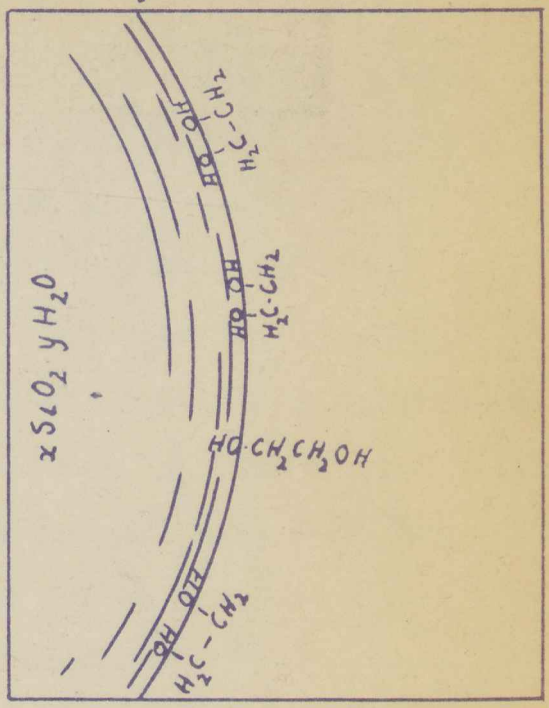
Figure 12.

Effect of non-Electrolytes — Sensitization

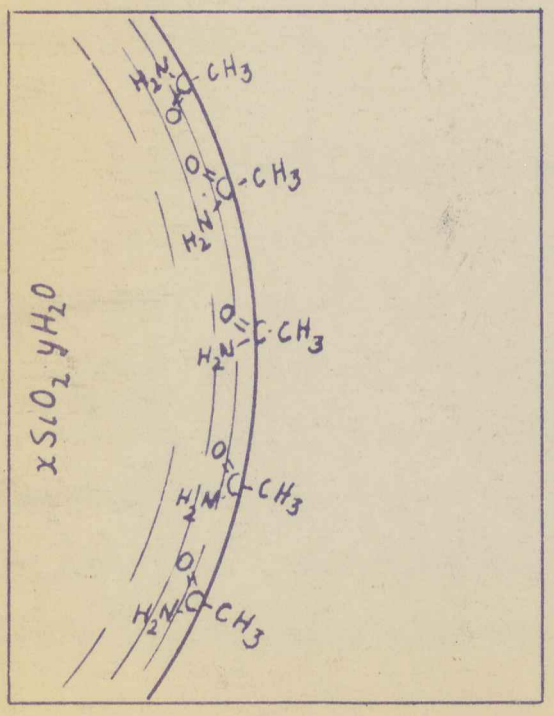
a. Ethyl Alcohol



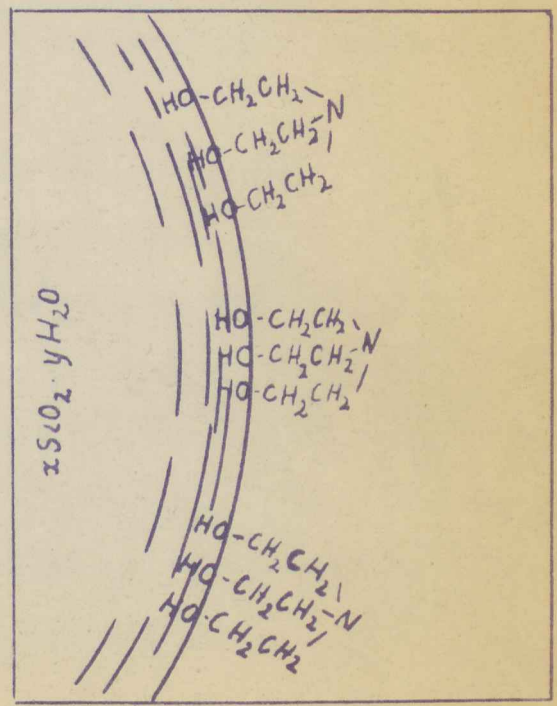
b. Ethylene Glycol



c. Acetamide



d. Triethanolamine



IX. "Ludox" and Hydrophilic Colloids

In studying the effect of hydrophilic substances on "Ludox" we have observed a phenomenon that is not encountered too frequently in connection with the interaction of hydrophilic and hydrophobic colloids. As a rule hydrophilic colloids, typified by gelatin, agar, tannin, and gum arabic, tend to protect hydrophobic sols. But in every case studied these colloids either sensitized "Ludox" or had no effect upon it. Not even the slightest indication of protection was obtained in any of the numerous types of experiments conducted on these "protective" colloids.

Sensitization by gelatin, tannin, albumins and other hydrophiles has been observed in a number of cases and Freundlich explains some of these cases very nicely (16). Generally, however, the type of sensitization which Freundlich discusses occurs only at very low concentrations of the hydrophiles (<.01%). The sensitization that we observed for the various substances mentioned above occurred in concentrations as high as 5%.

The manner in which we observe sensitization of "Ludox" by these hydrophilic substances is the same as that noted in connection with the study of non-electrolytes (Section VIII.) i.e. here again sensitization means sensitization toward electrolytes, potassium chloride in particular. The procedure is modified slightly in that the hydrophiles must be peptized in hot water; and the potassium chloride solutions are prepared in the respective hydrophilic sols to be used.

The extent of sensitization of "Ludox" by these hydrophilic colloids is brought out in Table 14 and in Figure 13.

Experiments conducted at the normal pH value for "Ludox" indicate sensitization of "Ludox" by these substances but no mutual coagulation in the absence of electrolytes. We have already mentioned (p.32) that at a low pH (3.42) gelatin and "Ludox" are mutually precipitated. We know that gelatin is positive at this pH, and from the discussion in Section V. we are of the opinion that "Ludox" is still negative at this pH. If this is so then the precipitation phenomenon is explainable on the basis of a discharge of oppositely charged sols. But at higher pH values both sols should be negative and the widespread occurence of sensitization can't be explained by a theory involving mutual discharge. This holds for the other hydrophilic colloids as well as for gelatin.

Protection by hydrophiles such as gelatin is explained on the assumption that the hydrophilic particles coat the particles in a hydrophobic sol giving them a more hydrophilic nature and stabilization of the hydrophobic sol results. The mechanism that we wish to propose for the sensitization of "Ludox" by hydrophiles, say gelatin, is that the silica particles are smaller than the gelatin particles; and instead of the gelatin coating the silica, the smaller silica particles attach themselves to the surface of the relatively large gelatin particles.

This process tends to produce a sol, still hydrophobic in nature, with a much larger particle size. Such a sol would be less stable toward electrolytes than the original and would in this way be sensitized.

Sensitization of this type has been mentioned in connection with the action of gelatin on gold sols (17); and it is interesting to observe that as far back as 1862 Graham (18) observed a mutual precipitation of silicic acid and gelatin. Elliott and Sheppard (19) have also shown that the protective action of gelatin depends upon the particle size which in turn depends upon the concentration of the gelatin sol and upon the manner of preparation. Following the procedure suggested by Elliott and Sheppard we prepared a gelatin sol of very low concentration (.002%) and in such a manner that we should have obtained the smallest particle size for the gelatin. Using such a sol we hoped to obtain "protection" in which case the gelatin would have coated the silica. The results that we obtained for this run, however, show nothing conclusive since the gelation curve for this determination nearly coincides with the standard curve in Figure 13.

As far as actual particle sizes are concerned, a value of 14.9 mμ has been obtained for the average diameter of the silica particles in "Ludox" sol (20) and there is some reason to believe that gelatin particles may swell to a size as great as 100 mμ (21). Further studies on the effect of hydrophiles could take the form of devising experiments to test the above theory. It could perhaps be possible with a suitable choice of conditions to obtain protection in some cases.

Table 14:

Effect of Hydrophilic Colloids

Gelatin

Conc. of KCl in Final Mixture (millimols/l.)	Gelation Time when the Indicated Gelatin Concentration is Present in the Mixtures		
	a) 1%	b) 0.05%	c) Standard (H_2O)
500	inst. ppt.	2-3 min.	3-4 min.
417	"	8-10 min.	10 min.
357	"	20-25 min.	32 min.
313	"	55-65 min.	1 hr. 10 min.
278	"	2-2½ hr.	3 hr.

Agar

Conc. of KCl in Final Mixture (millimols/l.)	Gelation Time when the Indicated Agar Concentration is Present in the Mixtures		
	a) 1%	b) 0.1%	c) Standard (H_2O)
500	inst.	2-2½ min.	3-4 min.
417	1-2 min.	7 min.	10 min.
357	2-3 min.	20-25 min.	32 min.
313	~ 15(?) min.	50 min.	1 hr. 10 min.
278	~ 5 min.	2 hr.	3 hr.

Concentration of SiO_2 in the gels $\simeq$ 7.5%

Table 14: (Cont'd)

Effect of Hydrophilic Colloids

Gum Arabic

Conc. of KCl in Final Mixture (millimols/l.)	Gelation Time when the Indicated Gum Arabic Concentration is Present in the Mixtures		
	a) 1%	b) 0.1%	c) Standard (H_2O)
500	½ min.	3 min.	3-4 min.
417	1-2 min.	10 min.	10 min.
357	3 min.	27 min.	32 min.
313	7 min.	55-60 min.	1 hr. 10 min.
278	15 min.	2½ hr.	3 hr.

Tannin

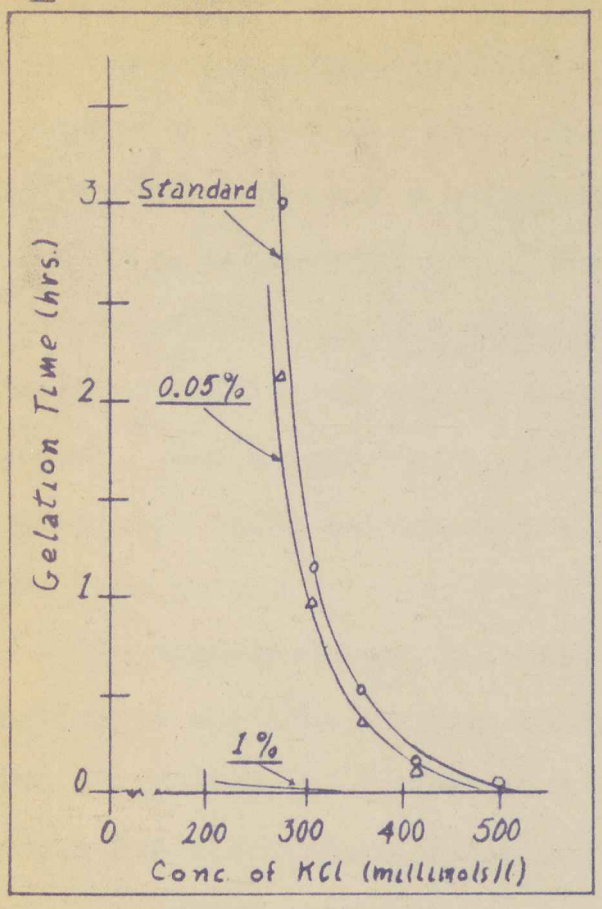
Conc. of KCl in Final Mixture (millimols/l.)	Gelation Time when the Indicated Tannin Concentration is Present in the Mixtures		
	a) 1%	b) 0.1%	c) Standard (H_2O)
500	inst. ppt. instead of gel	3 min.	3-4 min.
417		10 min.	10 min.
357	"	29-30 min.	32 min.
313	"	1 hr 10 min.	1 hr. 10 min.
278	"	-----	3 hr.

Concentration of SiO_2 in the gels $\simeq$ 7.5%

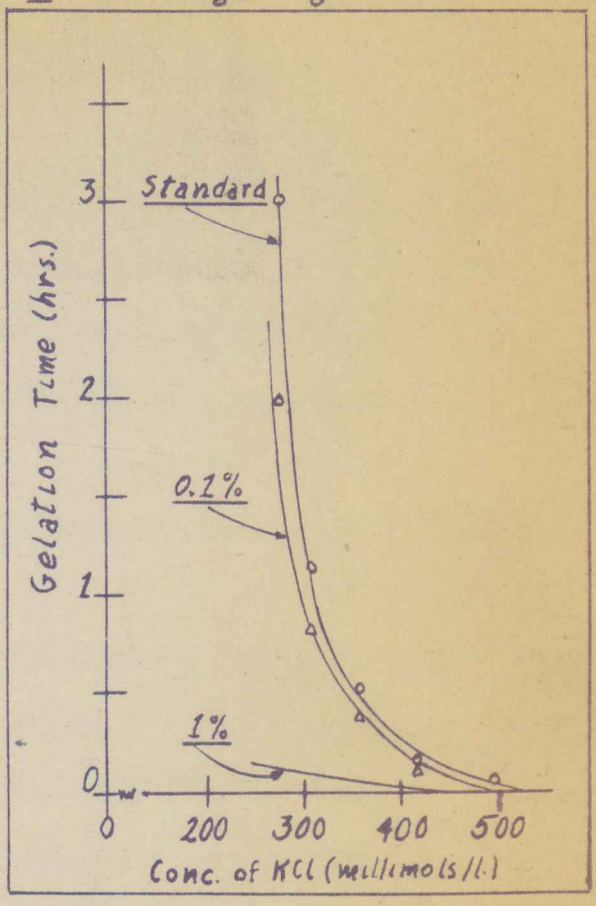
Figure 13.

Effect of Hydrophilic Colloids

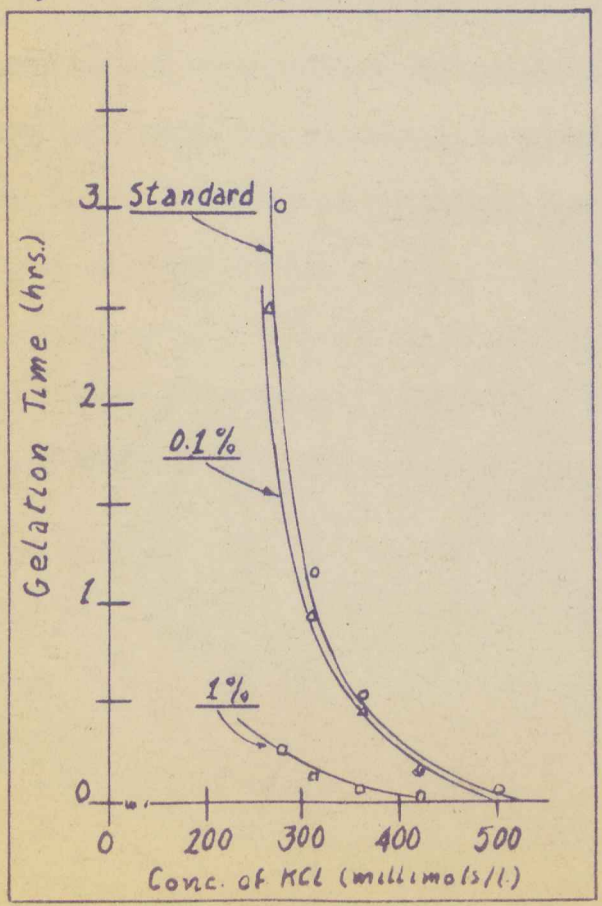
a. Gelatin



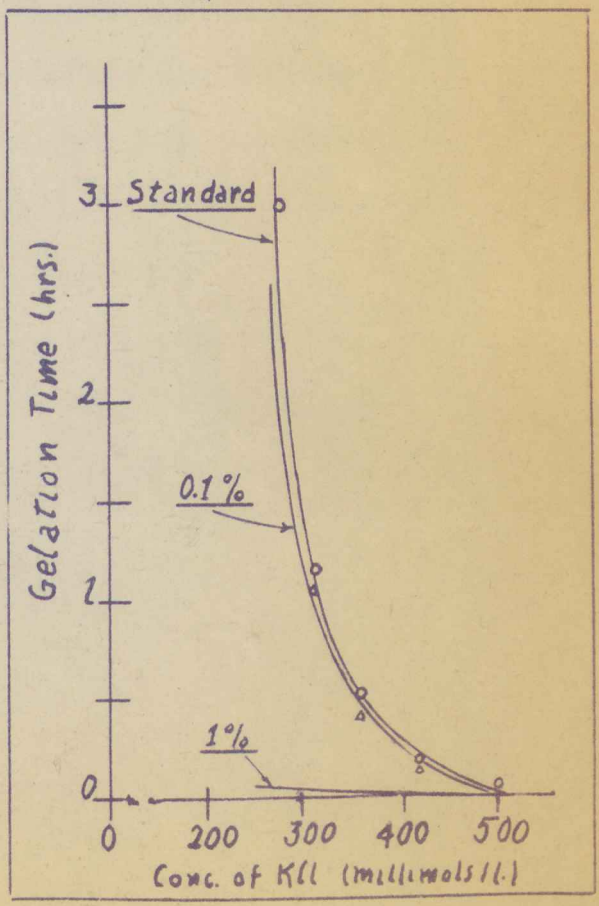
b. Agar-Agar



c. Gum Arabic



d. Tannin



X. Effect of Temperature on the Gelation of "Ludox"

We have attacked the problem of temperature effects by studying the manner in which gelation rates vary with temperature. Since the gelation of "Ludox" is comparable to other types of rate reactions, it was thought that the Arrhenius equation might apply here and that a definite energy of activation may be associated with the gelation process. The greater part of Section X, then, is concerned with a discussion of the experiments performed to test this point.

The procedure used in obtaining the gelation rates is similar to one that we have followed in previous experiments: Five milliliters of "Ludox" and five milliliters of the respective electrolyte solution being studied are pipetted into test tubes at room temperature. The solutions are then put into a constant temperature bath maintained at the particular temperature being studied. After the solutions have all come to constant temperature, they are mixed with the "Ludox" (also at constant temperature) and the gelation times are recorded.

Tables 15 and 16 show the gelation times for the various solutions of potassium chloride and magnesium chloride over the temperature range studied.

These data are represented graphically in Figures 14 and 15, where we have plotted the gelation time against the concentration of electrolyte in the gels on isotherms corresponding to the temperatures studied. We have also put our data on a logarithmic basis in Figures 16 and 17 so that we might apply the Arrhenius equation (See Appendix III. for the calculation, errors, and general discussion of the method involved). The results obtained in the calculation of activation energies appear in Table 19. Also included in Table 19 is the value that was obtained by Hurd and Miller (22) for the energy of activation in the gelation of mixtures of sodium silicate and acetic acid. This value is seen to correspond quite clearly to our value for the energy of activation in the gelation of magnesium chloride.

One of the factors to be noted in this study is that the rates of gelation with potassium chloride do not drop off between 25° and 4°C while those with magnesium chloride decrease very rapidly as the temperature is decreased. Thus the activation energies given in Table 19 for gelation by potassium chloride only apply above 25°C. The reason for this discrepancy, which may be something significant, is not at all apparent at the present time and there is room here for further investigation. The large experimental errors, which must be reduced before truly quantitative measurements on activation energies are possible, are outlined in Appendix III.

Table 15:

Effect of Temperature on Gelation by KCl

Conc. of KCl in Final Mixture (millimols/l.)	Gelation Time at the Indicated Temperature		
	4±1°C	10.0±.2°C	25.0±.3°C
357	5 min.	5-6 min.	7 min.
313	13 min.	15 min.	18 min.
278	35 min.	40 min.	37 min.
250	60-70 min.	1 hr. 30 min.	1 hr. 20 min.
227	3 hr.	2 hr. 40 min.	2 hr. 25 min.
208	6 hr.	5½-6 hr.	4 hr.

Conc. of KCl in Final Mixture (millimols/l.)	Gelation Time at the Indicated Temperature		
	40.0±.2°C	60±1°C	80±1°C
357	2-3 min.	~2 min.	~½ min.
313	10 min.	3-4 min.	1 min.
278	20 min.	~7 min.	1-2 min.
250	40 min.	12 min.	2-3 min.
227	1 hr. 5 min.	20 min.	4 min.
208	2 hr.	35 min.	10 min.

Concentration of SiO_2 in the gels ≃15%

Figure 14.

Effect of Temperature — Gelation by KCl

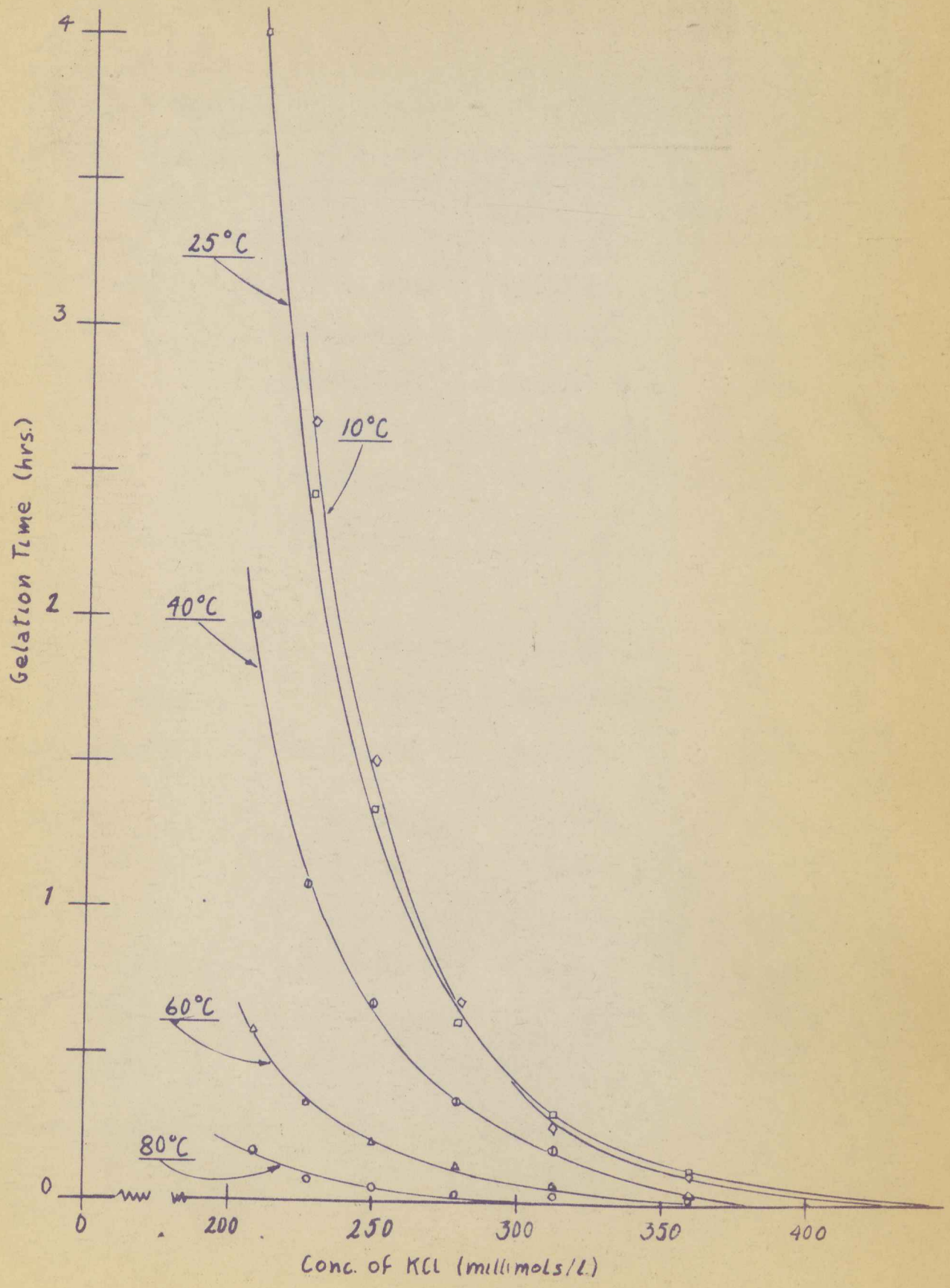


Table 16:

Effect of Temperature on Gelation by $MgCl_2 \cdot 6H_2O$

Conc. of $MgCl_2 \cdot 6H_2O$ in Final Mixture (millimols/l.)	Gelation Time at the Indicated Temperature		
	4±1°C	10.0±.2°C	25.0±.3°C
20.8	30-40 min.	16-18 min.	1-2 min.
20.0	2½-3 hr.	35-40 min.	4 min.
19.2	5½-6 hr.	1 hr. 40 min.	13 min.
18.5	15-17 hr.	3 hr. 40 min.	42 min.
17.9	25-30 hr.	~12 hr.	2 hr. 20 min.
17.2	50-60 hr.	---	6-7 hr.

Conc. of $MgCl_2 \cdot 6H_2O$ in Final Mixture (millimols/l.)	Gelation Time at the Indicated Temperature		
	40.0±.2°C	60±1°C	80±1°C
20.8	~2 min.	~½ min.	~½ min.
20.0	~3 min.	~½ min.	~½ min.
19.2	7 min.	1 min.	1 min.
18.5	12 min.	5 min.	1 min.
17.9	27 min.	15 min.	12 min.
17.2	1 hr 25-30 min.	35 min.	---

Concentration of SiO_2 in the gels ≃ 15%

Figure 15.

Effect of Temperature — Gelation by $MgCl_2 \cdot 6H_2O$

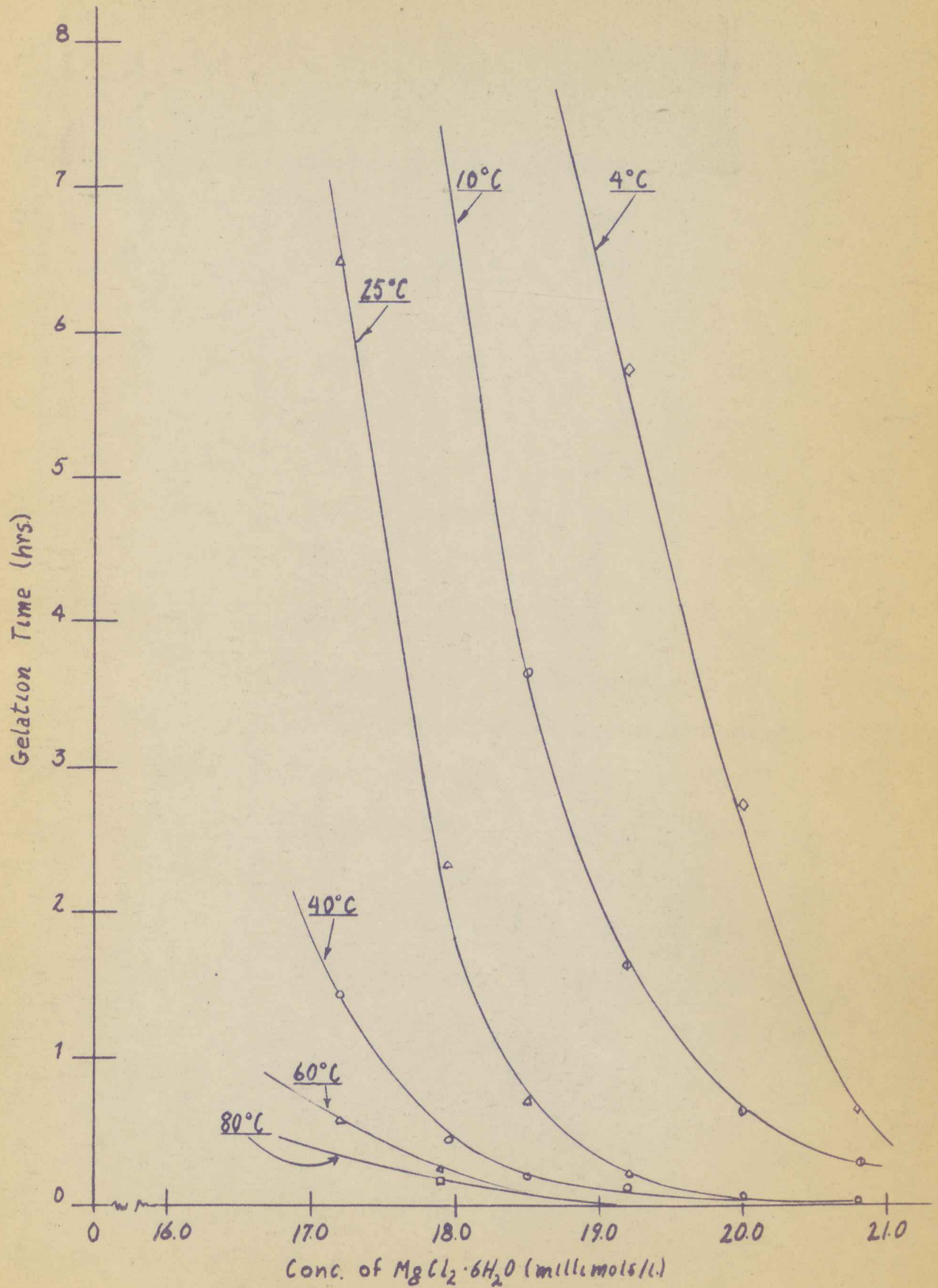


Table 17:

Effect of Temperature - Data for Figure 16

KCl

T (°K)	1/T x10³	(1) c = 357		(2) c = 313		(3) c = 278	
		Gelation Time (hr.)	Inverse Gelation Time (∝k)	Gelation Time (hr.)	Inverse Gelation Time (∝k)	Gelation Time (hr.)	Inverse Gelation Time (∝k)
277	3.61	.083	12.0	.22	4.6	.58	1.7
283	3.54	.092	10.9	.25	4.0	.67	1.5
298	3.36	.12	8.3	.30	3.3	.62	1.6
313	3.20	.042	24	.17	6.0	.33	3.0
333	3.00	.033	30	.058	17	.12	8.3
353	2.83	.0083	120	.017	60	.025	40

T (°K)	1/T x10³	(4) c = 250		(5) c = 227		(6) c = 208	
		Gelation Time (hr.)	Inverse Gelation Time (∝k)	Gelation Time (hr.)	Inverse Gelation Time (∝k)	Gelation Time (hr.)	Inverse Gelation Time (∝k)
277	3.61	1.08	.93	3.00	.33	6.00	.17
283	3.54	1.50	.67	2.67	.37	5.75	.17
298	3.36	1.33	.75	2.42	.41	4.00	.25
313	3.20	.67	1.50	1.08	.93	2.00	.50
333	3.00	.20	5.0	.33	3.00	.58	1.72
353	2.83	.042	24	.067	15	.17	6.0

c = conc. of KCl in gelation mixtures (millimols/l.)
∝k = a quantity proportional to the rate constant, k.

Concentration of SiO_2 in the gels ≃ 15%

Figure 16.

The Arrhenius Equation: Gelation of "Ludox" by KCl

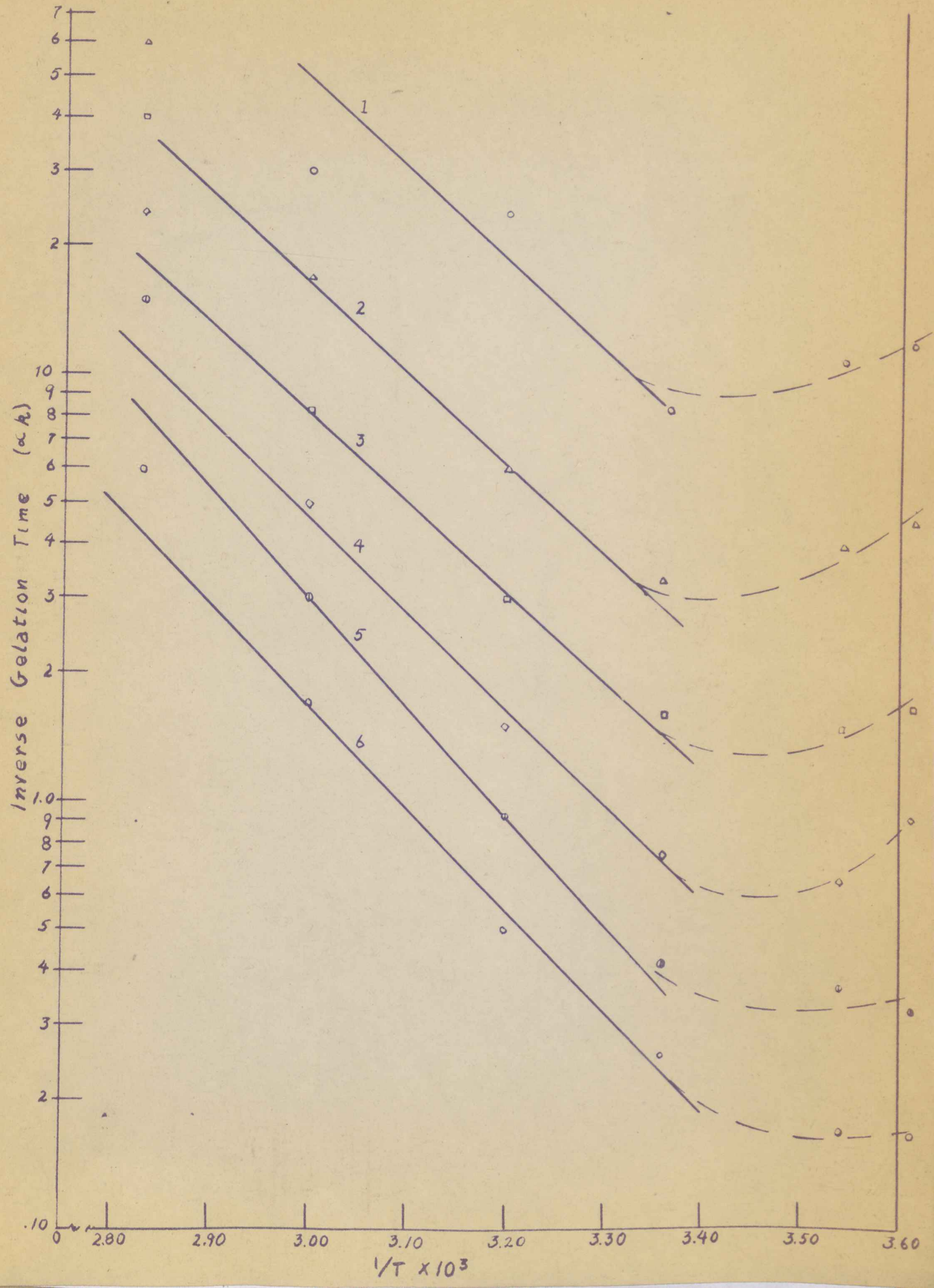


Figure 17.

The Arrhenius Equation: Gelation of "Ludox" by $MgCl_2 \cdot 6H_2O$

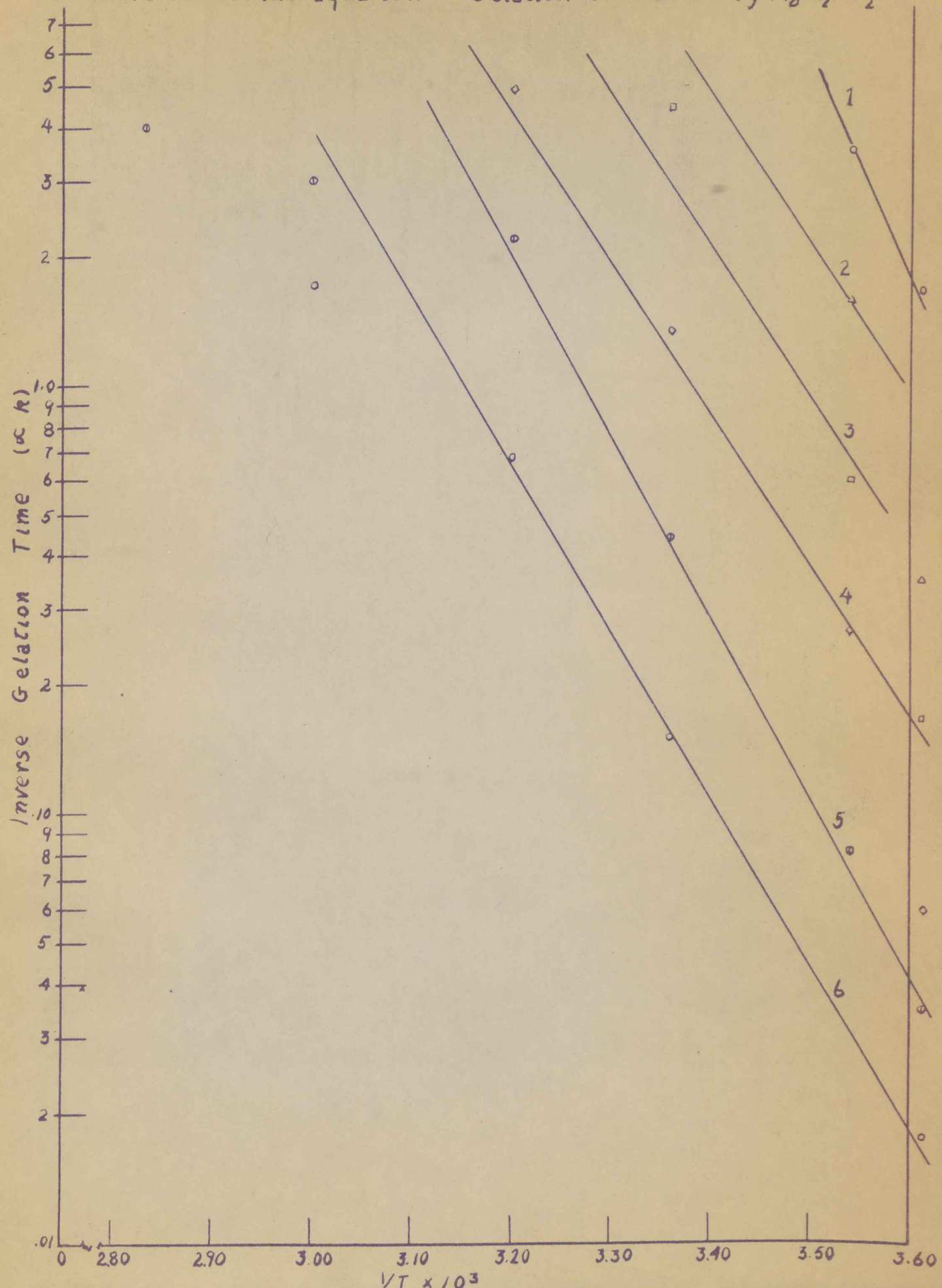


Table 19:

Activation Energies for the Gelation of "Ludox"

KCl

Line Number	Conc. of KCl in the Gels	Slope of Line	Activation Energy ΔH_a
1	357 millimols/l.	----	-----
2	313	-2,100	9,600 calories
3	278	-2,080	9,500
4	250	-2,220	10,200
5	227	-2,530	11,600
6	208	-2,350	10,800

Average value for ΔH_a = 10,300 calories

$MgCl_2 \cdot 6H_2O$

Line Number	Conc. of $MgCl_2$ in the Gels	Slope of Line	Activation Energy ΔH_a
1	20.8 millimols/l.	----	-----
2	20.0	----	-----
3	19.2	-3,500	16,000 calories
4	18.5	-3,520	16,100
5	17.9	-4,160	19,100
6	17.2	-3,840	17,600

Average value for ΔH_a = 17,200 calories

For silicic acid gels (22) ΔH_a = 16,640 calories

XI. Double Refraction in "Ludox" Gels

Perhaps the most interesting observation that was made in this study on "Ludox" sol was that of a very specific type of double refraction. Streaming double refraction in colloids is a common enough occurence but double refraction in gels is much less frequently observed. The work that we performed in this connection was initiated after reading a paper by Thiele and Lück (23) dealing with double refraction in various gels (eg. V_2O_5 and Fe_2O_3).

In looking for double refraction in "Ludox" gels the procedure of Thiele and Lück may be followed:

A little "Ludox" is poured into a small beaker and a crystal of the particular solute whose effect is being studied is dropped into the shallow layer of "Ludox". The beaker is then covered and set aside. As ions diffuse into the sol from the crystal, gelation begins and the gelled layer of "Ludox" extends outward from the electrolyte crystal and eventually covers the entire bottom of the beaker.

The beaker with its contents is now observed between crossed Polaroids under a strong beam of parallel illumination. If the gel is perfectly isotropic, no light will pass through the second Polaroid and the gel appears to be a deep violet color. If any anisotropy exists in the gel, however, the anisotropic portions will transmit light and will appear transparent. In carrying out such studies this is what was observed:

If the crystal introduced into the original sol is some magnesium salt, such as magnesium chloride, a very striking double refraction shows up in the final gel. The double refraction resembles that of a uniaxial crystal and is confined to a circular disc of gel around the crystal. (The pattern referred to here, that of a uniaxial crystal, shows up as a dark cross surrounded by a light area.) With the various other electrolytes used, very little, if any, double refraction was noted. Table 20 lists the electrolytes studied and the results obtained. Some of the electrolytes used in studies of this type failed to produce gelation (because of insolubility of the crystal or some other factor) and these are indicated in Table 20.

In explaining the double refraction which they observed in gels, Thiele and Lück make use of the differences in rates of diffusion of the anions and cations. Depending upon which ion diffuses the more rapidly, different types of orientation are possible with a subsequent difference in the sign of the double refraction (positive or negative). If this theory holds for the double refraction observed in "Ludox" gels, there should be closer agreement between salts which bring about double refraction and the transference numbers of the ions which they contain.

We can offer no explanation at this point for the fact that only magnesium salts exhibit this phenomenon so markedly. One observation made previously that may or may not have any bearing on this point is that magnesium salts produce the most transparent gels of any of the electrolytes studied. Also because double refraction, where it was known to occur, showed

up so weakly under a microscope, we were unable to determine the sign of the double refraction.

We hope that we have conveyed to the reader the very interesting nature of this problem and we believe that a continuation of this study should prove extremely profitable. It is with this idea in mind that we have compiled a list of literature references (see Appendix IV.) which we think may have some bearing on the problem. We are sure that at least some of these references will be valuable to future workers who will wish to enter into the study of double refraction in gels. (The reader will notice that we have included a few references which may not seem to have a direct bearing on the type of double refraction under discussion here. These references however contain the theory involved in other types of double refraction, such as streaming double refraction, and the reader may be able to obtain considerable information from them which should prove useful.)

Table 20:

Double Refraction in "Ludox" Gels

Electrolyte Studied	Results
magnesium chloride	+
" nitrate	+
" sulfate	+
" citrate	no gelation
" formate	+
" acetate	+
" borate	no gelation
" phosphate	-
calcium chloride	±
" nitrate	±
barium chloride	-
aluminum chloride	-
" sulfate	-

Electrolyte Studied	Results
sodium hydroxide	±
" chloride	±
" bisulfate	no gelation
" nitrate	±
potassium chloride	-
" ferrocyanide	-
" bromate	-
" hydroxide	-
lithium chloride	-
tartaric acid	-
trichloroacetic acid	no gelation
ammonium chloride	-
ferric chloride	-

+ = definite double refraction

± = slight evidences of double refraction

- = no double refraction

XII. Suggestions for Future Work

We have tried to suggest, throughout this paper, the direction that future workers in this field may take. Since "Ludox" is such a new product, there is still very much work to be done on it and the reader has probably seen possibilities for extension of our work that we have not specifically mentioned. One point that we should like to bring out is that the composition of "Ludox" varies from one batch to another (Some evidence of this was noticed in our work where we used three different samples of "Ludox".), and for the more quantitative studies it is advisable to use "Ludox" all from the same lot.

Let us recapitulate now and list those topics which are most worthy of future study:

1) Double refraction in "Ludox" gels (with special reference to magnesium salts).
2) Electrophoretic studies at various pH values with the purpose of determining the sign of the charge on "Ludox".
3) Quantitative electrophoretic measurements, combined with data on viscosity, dielectric constants, etc. to give a value for the ζ-potential of "Ludox".
4) Experiments with chromium nitrate in buffered "Ludox" sols to establish a relationship between "irregular-series" and pH.

5) Further studies on the system: SiO_2 - H_2O - C_2H_5OH to give data capable of representation on triangular phase diagrams.

6) Further studies on the effect of temperature with special reference to the anomalous behavior of potassium chloride at low temperatures.

7) Experiments on the interaction of hydrophilic substances and "Ludox" to test the theory of Section IX.

8) Experiments on non-electrolytes, especially of the mono-ethanolamine type, to test the adsorption hypothesis for non-electrolytes.

9) Further studies with trivalent cations, such as Al^{+++} with the possible analysis of some of the complex mixtures obtained.

10) Extension of our work on electrolytes to test the effect of more ions, both cations and anions, and especially to study some of the organic ions.

Appendix I. Approximate Calculation for the Distribution of Hydrogen Ions in "Ludox" Sol at Various pH Values

A typical acid sol was prepared by the addition of hydrochloric acid to "Ludox" and a reading of 5.01 was obtained on the Beckman pH Meter (see Table 21).

Table 21:

Preparation of Sol with pH 5.01

Vol. of Original "Ludox"	Vol. of 6N HCl	pH (Meter Reading)
40.0 ml.	1.0 ml.	5.01

Now let's calculate the pH of the solution resulting from the addition of one milliliter of 6N HCl to 40 milliliters of water (The volume of 6N HCl required to bring a solution from a pH of 10 to 7 is almost negligible as far as this calculation is concerned):

$$c_{H^+} \quad \frac{6 \times 1 \text{ meq.}}{41 \text{ ml.}} = .015M \qquad pH = 1.8$$

This calculation shows that nearly all of the hydrogen ion has been in some way removed so that it is no longer reversible to a glass electrode. Hydrogen ions within the double layers of micelles will not register on a pH meter and hence, as was pointed out in Section V., there may well be a very strong adsorption of hydrogen ions by the silica particles.

Appendix II. Notes on the Calculation of SiO_2 Concentrations

The reader has probably noticed that in many of the tables the silica concentrations in the sols and gels are indicated as approximate quantities (eg. conc. of $SiO_2 \simeq 30\%$, conc. of $SiO_2 \simeq 15\%$ etc.). These concentrations have been calculated on the assumption that when a given volume of "Ludox" is mixed with an equal volume of some other solution, the resulting mixture has the same density as the original "Ludox" (i.e. that the added solution has the same density as the "Ludox"). A mixture of equal volumes of "Ludox" and another solution under these conditions would have exactly half the silica concentration by weight of the original sol. Thus by our method, on mixing equal volumes of "Ludox" and an electrolyte we say that the concentration of silica in the gel $\simeq 15\%$. Similarly four-fold dilution gives us $\simeq 7.5\%$ silica.

But of course this situation rarely exists, for by and large, the densities of "Ludox" and of the particular solution mixed with it are not equal. The following problem will illustrate how large our error is in making this assumption:

In Table 2, 5.00 ml. of the first member of the first series (i.e. 1.00M KCl) are added to 5.00 ml. of "Ludox". Assuming the SiO_2 concentration in "Ludox" to be 30%, its density to be 1.21 g/cc. and the density of 1.00M KCl equal to 1.04 g/cc., what is the SiO_2 concentration in the final mixture?

In 5.00 ml. of "Ludox", we have: $.30 \times 5.00 \times 1.21 = 1.82$g. of SiO_2. The total weight of the final mixture $= 5 \times 1.21 + 5 \times 1.04 = 11.25$g. Then the $\%SiO_2 = 1.82/11.25 = 16.1$ as compared to 15% by assuming constant density.

This calculation shows that, strictly speaking, the concentrations that are expressed throughout this paper may be in slight error; but since we do not know exactly what the silica concentration is in the original sol, and since each time a mixture is prepared it would be necessary to calculate the silica concentrations on the basis of the densities of the solutions used, we believe that at least for a preliminary study such as this our assumption is justified.

In one case, however, we find that it is necessary to make allowances for the difference in densities of the sol and the solutions with which it is mixed. This is in connection with the data in Figure 8 on the gelation by ethyl alcohol. Since ethyl alcohol has a density considerably below that of "Ludox", the errors in our assumption would be considerable. The following typical calculation shows how one may determine the silica concentration in a mixture of "Ludox" and ethyl alcohol:

Ex: 100 ml. of 60% EtOH (by vol.) is added to 100ml. of "Ludox".
Density of "Ludox" = 1.21 g./cc.
Density of EtOH = .914 g./cc.

The weight of SiO_2 = .30 x 1.21 x 100 = 36.3 g.

The total weight of the mixture = 100 x 1.21 + 100 x .914 = 212.4 g.

$\%SiO_2 = 36.3/212.4$

$\%SiO_2 = 17.1\%$

Appendix III. The Arrhenius Equation -- Calculation of Activation Energies

Since the greater part of Section X. deals with the presentation of data for use in the Arrhenius equation, it seems advisable to discuss at this point the Arrhenius equation, its application to the gelation of "Ludox", and some of the errors involved.

The logarithmic form of the Arrhenius equation is:

$$\log k = \frac{\Delta Ha}{2.303RT} \text{ constant}$$

where:

K = the rate constant of the reaction being studied

ΔH_a = activation energy in calories

R = molar gas constant = 1.987 calories/mole deg.

T = absolute temperature

By plotting: log k vs. 1/T one should obtain a straight line if the reaction studied follows the Arrhenius equation. The intercept of the straight line gives an evaluation of the constant term, and the slope of the line gives the value of: $\Delta Ha/2.303R$. Figures 16 and 17 represent our data for temperature studies plotted on three-cycle semi-log paper. Those lines which extend for more than three cycles were plotted by attaching a further three cycles above. In the final graphs, however, only the three lower cycles are shown.

Now that we have set the Arrhenius equation in its proper background, let us apply it to the calculation of the activation energies from Figures 16 and 17. As a typical example we may work with line 3 in Figure 16 which represents data on the temperature studies with gelation caused by .278 M potassium chloride:

Line 3 cuts the 1.0 cycle at a 1/T value of .003435 and the 10 cycle at .002955. The difference in logarithms for these two cycles is 1.00 and the difference in the 1/T intercepts is: .002955 - .003435 = -.000480. This gives us a slope of -2,080 for line 3.

The Arrhenius equation tells us that:

$$\text{slope} = \frac{\Delta H_a}{2.303R} \qquad -\Delta H_a = 2.303R \times \text{slope}$$

Thus for line 3:

$\Delta H_a = -2.303R \times \text{slope}$

$\Delta H_a = 2.303 \times 1.987 \times 2{,}080$

$\Delta H_a = 9{,}500$ calories

The errors involved in a quantitative application of the Arrhenius equation to the gelation of "Ludox" are considerable because of the manner in which the data have to be obtained. To illustrate how a very slight error in observing gelation times may show up greatly in the plotting of the data let us look at line 2 of Figure 16. From Table 17 at a temperature of 80°C (1/T = .00283) the gelation time given for this concentration of potassium chloride is .017 hours (1 min.). With gelation as rapid as this, however, large errors can occur; for in this case the gelation time might just as well have been ½ min. or 1½ min. This means that an inverse gelation time of 60 might actually be anywhere from 40 to 120.

There isn't too much that can be done to avoid this particular difficulty; for if the experiments are performed under conditions in which gelation is very rapid, the errors involved are large. The best manner in which to obtain more quantitative results would be to select temperature ranges and electrolyte concentrations such that the gelation times fall within the range of 15 minutes to 5 or 6 hours. In this way errors of the type mentioned above could be avoided.

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